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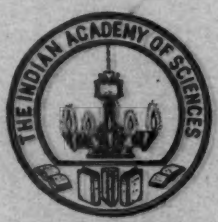

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ON THE ADDITION OF RESIDUE CLASSES.

By S. S. Pillai.

(From the Department of Mathematics, Annamalai University, Annamalainagar, S. India.)

Received December 13, 1937.
(Communicated by Dr. S. Chowla.)

§1. M is a positive integer. Unless otherwise mentioned, 'residue classes' means 'different residue classes modulus M'. (a, b) is the greatest common divisor of a and b. $a_1, a_2, \cdots, a_m$; and $b_1, \cdots, b_n$ are two sets of residue classes; $c_1, c_2, \cdots, c_l$ are the residue classes which can be represented in the form

$$a_i + b_j,\ 1 \leqslant i \leqslant m,\ 1 \leqslant j \leqslant n.$$

L, is the residue classes of the forms

$$a_i \text{ or } a_i + b_j,\ 1 \leqslant i \leqslant m,\ 1 \leqslant j \leqslant n$$

$$d_r = (\mathrm{M}, b_1 - b_{r+1}),\ r = 1, \cdots, n-1.$$

Without loss of generality, we can assume that the suffixes of b's are so ordered that $d_r \leqslant d_{r+1}$, $(r = 1, \cdots, n-2)$, and d_{n-2} assumes its least possible value.

$$\mathrm{H} = \text{Min.}\ \left\{\frac{\mathrm{M}}{d_1}, \frac{\mathrm{M}}{d_2} + 1, \cdots, \frac{\mathrm{M}}{d_{n-1}} + n - 2\right\}.$$

The object of this note is to prove the following:

Theorem 1. When $m + n - 1 \leqslant \mathrm{H}$,

$$l \geqslant m + n - 1.$$

Theorem 2. When $m + n - 1 \geqslant \mathrm{M}$,

$$l = \mathrm{M}.$$

The following results are either particular cases of or immediate corollaries to the above theorems.

Theorem 3. When $m + n - 1 \leqslant \mathrm{M}/d_{n-1}$,

$$l \geqslant m + n - 1.$$

Theorem 4. (Davenport.)[1] If M is a prime, then when $m + n - 1 \leqslant \mathrm{M}$, $l \geqslant m + n - 1$.

Theorem 5. (I. Chowla.)[2] If $(\mathrm{M}, b_j) = 1$, $1 \leqslant j \leqslant n$, then when $m + n$ M, $\leqslant \mathrm{I}, \geqslant m + n$.

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[1] The *Journal of the London Mathematical Society*, **10**, Part 1, No. 37.

[2] Satz 114 in Cambridge Tracts, No. 35, by Landau.

THEOREM 6. If $(b_1, M) = 1$ and $(b_1 - b_r, M) = 1$, $2 \leqslant r \leqslant n$, then when $m + n \leqslant M$, $L_r \geqslant m + n$.

THEOREM 7. If no $b \equiv 0 \pmod{M}$ and $m + n \leqslant H$, then,

$$L_r \geqslant m + n.$$

This is a generalization of theorems 5 and 6.

THEOREM 8. If no $b \equiv 0 \pmod{M}$ and $m + n \geqslant M$,

then $$L_r = M.$$

This theorem is proved by I. Chowla,[3] with the restriction that all b's are prime to M.

THEOREM 9. If H_1 is defined with respect to $a_1, \cdots, a_m$ as H is defined with respect to $b_1, \cdots, b_n$; and $T = \text{Max. } \{H_1, H\}$, then when $m + n - 1 \leqslant T$, $l \geqslant m + n - 1$.

A weaker form of theorem 1 was proved by the author recently.[4]

It is interesting to note that when $M \leqslant m + n - 1$, to prove that $l = M$, we need put absolutely no restriction on the residue classes a's and b's.

In theorem 8, also, the restriction on b is very mild.

In my paper referred to above, the statement, when $m + n - 1 > \frac{M}{d}$ is not correct.

§ 2. To prove theorem 1, I follow Davenport. So it is by induction on n. For $n = 1$, there is nothing to prove.

Let $n = 2$. Consider

$$\text{(A)} \qquad \begin{cases} a_1 + b_1, a_2 + b_1, \cdots, a_m + b_1, \\ a_1 + b_2, \cdots\cdots\cdots, a_m + b_2 \end{cases}$$

$$a_r + b \not\equiv a_t + b \pmod{M}, \tag{1}$$

otherwise $a_r \equiv a_t$, which is not true.

$$a_r + b_1 \equiv a_t + b_2$$

and

$$a_s + b_1 \equiv a_t + b_2 \tag{2}$$

are impossible;

For, otherwise, by subtraction,

$a_r \equiv a_s$, which is not true.

Hence, if there are only m residue classes in (A),

$$a_r + b_1 \equiv a_t + b_2 \pmod{M},$$

where for every r, there is one unique t.

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[3] Satz 115 in Cambridge Tracts, No. 35, by Landau.

[4] This *Proceedings*, 1937, **6**, No. 3.

Therefore,

$$\sum_{r=1}^{m} (a_r + b_1) \equiv \sum_{t=1}^{m} (a_t + b_2), \pmod{M}.$$

So $$mb_1 \equiv mb_2, \pmod{M},$$

Consequently, $m \equiv 0, \left(\mod \cdot \frac{M}{(M, b_1 - b_2)}\right)$.

That is, $m \geqslant M/d_1$.

So if $m < M/d_1$, there will be at least $m + 1$ residue classes in (A). So the theorem is proved when $n = 2$.

Therefore, we can suppose that $n > 2$, and that the theorem is true for all $n' < n$. We apply the theorem to the two sets of residue classes $c_1, c_2, \cdots, c_l$; b_1, b_2. If $l \geqslant H$, there is nothing to prove. So we shall assume that $l < H$. Then there are at least $l + 1$ residue classes in

$$\text{(B)} \qquad \begin{cases} c_1 + b_1, \cdots, c_l + b_1 \\ c_1 + b_2, \cdots, c_l + b_2. \end{cases}$$

So there is a δ such that $\delta - b_2$ is a c and $\delta - b_1$ is not. Let $b_{k_1}, b_{k_2}, \cdots, b_{k_r}$ be the residue classes in order in the set $b_1, b_3, b_4, \cdots, b_n$, which are such that $\delta - b_{k_t}$ is not a c for $1 \leqslant t \leqslant r$, and for other b's $\delta - b$ is a c. Obviously, $b_{k_1} = b_1$ and $r < n$. Now when $b \neq b_{k_t}$, $\delta - b$ is a c. Since we can arrange $c_1, \cdots, c_l$ in any order we please, we may order the suffixes so that

$$\delta - b \equiv c_s, \text{ for } 1 \leqslant s \leqslant n - r,$$

where $b \neq b_{k_t}$.

Now none of the residue classes $c_s - b_{k_t}$ (where $1 \leqslant s \leqslant n - r$, $1 \leqslant t \leqslant r$) is an a. For, if so, we should have $c_s - b_{k_t} \equiv a$, that is,

$$a + b_{k_t} \equiv c_s = \delta - b, b \neq b_{k_t}, 1 \leqslant t \leqslant r,$$

i.e., $a + b \equiv \delta - b_{k_t} \not\equiv c$, which is not true. Therefore, the l' residue classes representable in the form $a_i + b_{k_t}$ $(1 \leqslant i \leqslant m,\ 1 \leqslant t \leqslant r)$ form a subset of c's not containing $c_1, c_2, \cdots, c_{n-r}$.

Thus $$l' \leqslant l - (n - r). \tag{3}$$

But by our theorem with $n' = r < n$,

$$l' \geqslant m + r - 1, \tag{4}$$

provided $$m + r - 1 \leqslant K, \tag{5}$$

where

$$K = \text{Min.} \left\{ \frac{M}{(M, b_1 - b_{k_2})}, \frac{M}{(M, b_1 - b_{k_3})} + 1, \cdots, \frac{M}{(M, b_1 - b_{k_r})} + r - 2 \right\}.$$

That is, $l' \geqslant m + r - 1$,

provided $$m + n - 1 \leqslant K + n - r. \tag{6}$$

Now, since $k_{t+s} \geqslant k_t + s$, $n - r \geqslant k_r - r \geqslant k_t - t$, $1 \leqslant t \leqslant r$.

So $$\frac{M}{(M, b_1 - b_{k_t})} + t - 2 + n - r \geqslant \frac{M}{(M, b_1 - b_{k_t})} + k_t - 2.$$

Therefore, $$K + n - r \geqslant H. \tag{7}$$

Hence from (6) and (7), we conclude that

if $$m + n - 1 \leqslant H, \text{ then } l' \geqslant m + r - 1. \tag{8}$$

So from (3) and (8), it follows that if $m + n - 1 \leqslant H$, then $l \geqslant m + n - 1$.

Thus theorem 1 is proved.

§ 3. Now we shall prove theorem 2. If theorem 2 is not true, there should be at least one residue class δ such that $\delta - b_j$ is not an a when $1 \leqslant j \leqslant n$. So $m + n \leqslant M$, which is against the hypothesis. Hence there is no δ of the above form. Therefore $l = M$.

§ 4. Theorem 3 is only a weaker form of theorem 1.

If M is a prime, $d_{n-1} = 1$. So theorem 4 is a particular case of theorem 3.

In order to prove theorem 5, consider the two sets of residue classes $a_1, \cdots, a_n$; and $0, b_1, b_2, \cdots, b_n$. Since by hypothesis, $(M, b_j) = 1$, for $1 \leqslant j \leqslant n$, $0, b_1, \cdots, b_n$ are all different and $(M, 0 - b_j) = 1$, $1 \leqslant j \leqslant n$. Hence $H = M$, and so from theorem 1, $I_r \geqslant m + n$; for, there are $n + 1$ residue classes in the second set.

To prove theorem 6, one has to consider the two sets of residue classes $a_1, \cdots, a_m$ and $b_1, b_2, \cdots, b_n, 0$. In this case $(M, b_1 - 0) = 1$ and $(M, b_1 - b_j) = 1$, $1 \leqslant j \leqslant n$. So $H = M$. Therefore $I_r \geqslant m + n$.

For theorem 7, consider $a_1, \cdots, a_m$; and $0, b_1, \cdots, b_n$ and apply theorem 1.

If theorem 8 is not true, there is a δ such that neither δ nor $\delta - b_j$ $(1 \leqslant j \leqslant n)$ is an a. So $m + n + 1 \leqslant M$, which is not true. So $I_r = M$.

Consideration of symmetry leads to theorem 9 from theorem 1.

ON CONICS CONNECTED WITH FOUR OR MORE LINES.

By F. C. Auluck.

(From the Department of Physics, Government College, Lahore.)

Received December 13, 1937.
(Communicated by Dr. S. Chowla.)

After V. Ramaswami Aiyer I define Γ_P as the conic passing through a point P and the feet of the perpendiculars from it on four given lines. In this paper I prove the following theorems :

Theorem I. *Given five lines* L_r $(1 \leqslant r \leqslant 5)$ *in a plane, the locus of a point* P *which moves so that* Γ_P, *associated with the lines* L_r $(2 \leqslant r \leqslant 5)$, *has one of its axes parallel to* L_1 *is a curve of the 5th degree consisting of the four lines* L_r $(2 \leqslant r \leqslant 5)$ *and another line* L_1'.

Proof.

Taking any point O on L_1 as the origin and the lines through O inclined at an angle $\frac{\pi}{4}$ with L_1 as the co-ordinate axes, we see that the axes of Γ_P must be parallel to the lines $x^2 - y^2 = 0$.

Let the equations of the four lines L_r $(2 \leqslant r \leqslant 5)$ be

$$L_r \equiv p_r - x \cos \alpha_r - y \sin \alpha_r = 0.$$

If the point P is (x, y), then the co-ordinates of the feet of the perpendiculars from P on the lines L_r are of the form (X_r, Y_r), where

$$X_r = x + L_r \cos \alpha_r, \quad Y_r = y + L_r \sin \alpha_r.$$

The equation of a conic having its axes parallel to $x^2 - y^2 = 0$ is

$$x^2 + 2hxy + y^2 + 2gx + 2fy + c = 0.$$

The point P and the four feet lie on this conic if

$$\begin{vmatrix} x^2 + y^2 & xy & x & y & 1 \\ X_2^2 + Y_2^2 & \cdot & \cdot & Y_2 & 1 \\ \cdot & \cdot & \cdot & \cdot & \cdot \\ X_5^2 + Y_5^2 & \cdot & \cdot & Y_5 & 1 \end{vmatrix} = 0$$

which immediately reduces to

$$L_2L_3L_4L_5 \begin{vmatrix} L_2 & L_2 \sin \alpha_2 \cos \alpha_2 & \cos \alpha_2 & \sin \alpha_2 \\ \cdot & \cdot & \cdot & \cdot \\ L_5 & L_5 \sin \alpha_5 \cos \alpha_5 & \cos \alpha_5 & \sin \alpha_5 \end{vmatrix} = 0$$

or, by adding x times the 3rd column and y times the 4th to the first column.

$$L_2L_3L_4L_5 \begin{vmatrix} p_2 & L_2 \sin a_2 \cos a_2 & \cos a_2 & \sin a_2 \\ . & . & . & . \\ p_5 & L_5 \sin a_5 \cos a_5 & \cos a_2 & \sin a_5 \end{vmatrix} = 0$$

a fifth degree equation consisting of the four lines themselves and a line L_1' (say).

2. THEOREM II. *The locus of a point* P *which moves so that* Γ_P, *associated with four given lines* L_r $(2 \leqslant r \leqslant 5)$, *has the property that the product of the tangents of the angles made by its asymptotes with a given line* L_1 *is constant, is a curve of the* 6*th degree consisting of the four lines* L_r $(2 \leqslant r \leqslant 5)$ *and a circle* C_1.

Proof.

Taking L_1 as the x-axis and the equations of the other lines as before we see that Γ_P is of the form

$$\lambda x^2 + 2hxy + y^2 + 2gx + 2fy + c = 0,$$

where λ is a constant.

Proceeding as before we see that P lies on the curve

$$L_2L_3L_4L_5 \begin{vmatrix} L_2(\lambda \cos^2 a_2 + \sin^2 a_2) & L_2 \cos a_2 \sin a_2 & \cos a_2 & \sin a_2 \\ . & . & . & . \\ L_5(\lambda \cos^2 a_5 + \sin^2 a_5) & L_5 \cos a_5 \sin a_5 & \cos a_5 & \sin a_5 \end{vmatrix} = 0$$

It is easily seen that coefficients of x^2 and y^2 in the determinant are equal and coefficient of xy is zero.

If $\lambda = -1$, we get V. Ramaswami Aiyer's theorem that if Γ_P is a rectangular hyperbola, the locus of P is the centre-circle of the four lines. Our result shows that the locus consists of the four lines themselves also.

From the above two theorems we easily obtain

THEOREM III. *Given a set of five lines, we can associate with them another set of five lines and an infinity of sets of five circles.*

I do not know if there is any relation between the two sets of five lines and in particular if the relation is a reciprocal one.

4. N. Durairajan has shown[1] that the locus of point which is such that the feet of the perpendiculars from it on the six lines lie on a conic is a curve of the 8th degree. I show that the curve is of the 7th degree.

[1] *The Mathematics Student*, 5. No. 1, pp. 29-30.

As before, we see that P lies on

$$\begin{vmatrix} L_1^2 \cos^2 a_1 & L_1^2 \cos a_1 \sin a_1 & L_1^2 \sin^2 a_1 & L_1 \cos a_1 & L_1 \sin a_1 & 1 \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ L_6^2 \cos^2 a_6 & \cdot & \cdot & \cdot & L_6 \sin a_6 & 1 \end{vmatrix} = 0$$

a curve of the 8th degree but the terms of the 8th degree are

$$\begin{vmatrix} P_1^2 & P_1Q_1 & Q_1^2 & P_1 & Q_1 & 1 \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ P_6^2 & P_6Q_6 & Q_6^2 & P_6 & Q_6 & 1 \end{vmatrix}$$

where

$$P_r = -(x \cos a_2 + y \sin a_r) \cos a_r$$
$$Q_r = -(x \cos a_r + y \sin a_r) \sin a_r.$$

Now

$$xP_r + yQ_r + P_r^2 + Q_r^2 = 0.$$

Hence the above determinant vanishes.

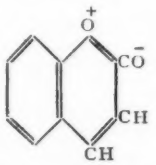
FIXATION OF THE AROMATIC DOUBLE BONDS IN THE COUMARIN RING SYSTEM.

By S. Rangaswami and T. R. Seshadri.

(From the Department of Chemistry, Andhra University, Waltair.)

Received December 18, 1937.

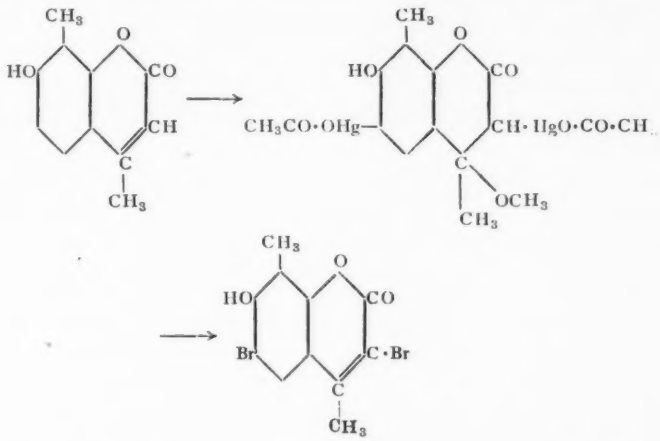
The idea that the double bonds of aromatic ring systems are not always capable of oscillation as originally conceived by Kekule and that in several cases they have a tendency to get fixed in certain favourable positions has been gaining increased acceptance during recent years. The factor producing this fixation seems to be the fusion with a second ring.[1] Naphthalene seems to exist only in the symmetrical form possessing a double bond common to the two rings and seems to be incapable of assuming the alternative structure.[2] That even the formation of chelate rings produces bond fixation has been shown by Baker.[3] A number of evidences indicate the existence of such a fixation in the coumarin molecule. A double bond seems to exist in common to the two rings and in this respect it seems to resemble naphthalene. From many chemical and physical considerations coumarin has been frequently given the following structure in which the two rings are aromatic.



Though in coumarin itself substitution invariably takes place in the sixth position, in 7-hydroxy-coumarin it is exclusively in the eighth position. When the hydroxyl group is involved in the formation of fresh rings such as the furan and the pyrone, almost invariably the angular variety is produced. The migration of the allyl group from the allyl ether of 4-methyl-7-hydroxycoumarin has been shown to be to the eighth position,[3] thus showing conclusively that there exists a double bond between the 7 and 8 positions. However in the pyrogenic conversion of the acetyl derivative (Fries) of the hydroxy compound[4] and in the formation of a fresh α-pyrone ring[5] it has been realised that the position 6 is to a small extent reactive. With a view to let in more definite evidence as to how far the double bonds of the benzene ring can assume the alternative positions, the method of Fieser[2&6] is here adopted.

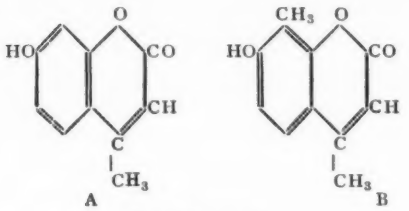
The position 8 is blocked by means of a methyl group and the reactivity of 7-hydroxy-4 : 8-dimethylcoumarin examined.

7-Hydroxy-4 : 8 dimethylcoumarin forms an acetyl derivative which undergoes the Fries rearrangment on heating with aluminium chloride to give a fair yield of 7-hydroxy-4 : 8-dimethyl-6-acetylcoumarin. The constitution of this and of several others described in this paper are deduced from well-known analogies and there exist no alternatives. 7-hydroxy-4 : 8-dimethylcoumarin reacts fairly easily with mercuric acetate in methyl alcoholic solution to produce a product in which addition at the double bond and mercuration in the benzene ring have taken place according to the general behaviour of coumarins already elucidated.[7] On treatment with bromine this mercury compound forms 7-hydroxy-4 : 8-dimethyl-3 : 6-dibromocoumarin.



The reaction of diazonium salts on the coumarin was examined in acetic acid medium since in an alkaline solution the pyrone ring will be opened out. The most reliable evidence is that obtained from the migration of the allyl group (Claisen's transformation). The allyloxycompound readily undergoes change on being heated to produce an allylhydroxydimethylcoumarin in good yield. The product is obviously 7-hydroxy-6-allyl-4 : 8-dimethylcoumarin.

From these and from results already recorded it is concluded that though coumarins react predominantly in the form (A) possessing a double bond between the two rings and consequently another between the 7 and 8 positions, reactivity in the isomeric form (B) is also possible and if the eighth position is blocked up by a methyl group reaction takes place fairly easily in the 6th position, the necessary shift in the double bonds having taken place.



Experimental.

7-*Hydroxy*-4 : 8-*dimethylcoumarin*[5] was prepared by condensing 2-methylresorcinol with ethylacetoacetate in the presence of sulphuric acid. On recrystallisation from alcohol it was obtained as thin plates melting at 258°.

7-*Acetoxy*-4 : 8-*dimethylcoumarin* was obtained by heating the hydroxy compound with acetic anhydride and sodium acetate for 4–5 hours. It crystallises from alcohol as thin plates and needles melting at 135–36°. It is insoluble in cold dilute ammonia and in sodium bicarbonate solution and gives no colouration with ferric chloride. (Found : C 67·0, H 5·2 ; $C_{13}H_{12}O_4$ requires C 67·2, H 5·2%.)

Fries rearrangement: 7-*hydroxy*-6-*acetyl*-4 : 8-*dimethylcoumarin*.— The above compound (0·2 g.) was intimately mixed with powdered anhydrous aluminium chloride (1 g.) and baked in an oil bath at 160° for one hour. After cooling the product was decomposed with dilute hydrochloric acid and the solid filtered. It was macerated with cold dilute ammonia which removed a small amount of impurity. The undissolved residue crystallised from alcohol as colourless fine needles melting at 192–93°. (Found : C 67·4, H 5·3 ; $C_{13}H_{12}O_4$ requires C·67·2 H 5·2%.) The yield was 0·1 g. and the compound gave a reddish violet colouration with alcoholic ferric chloride solution.

Action of mercuric acetate.—A solution of the hydroxydimethylcoumarin (0·5 g.) in methanol (50 c.c.) was mixed with a solution of mercuric acetate (2 g.) in methanol (15 c.c.) containing a few drops of acetic acid. A small precipitate was formed immediately. This was filtered and the clear filtrate heated under reflux for 6 hours. The solid that had separated was filtered while the mixture was hot and washed repeatedly with hot methanol and air dried—(yield 0·6 g.). By boiling the filtrate again more of the product could be obtained ; but it was not quite pure. The compound had no definite crystalline structure and decomposed slowly above 260°. It had no melting point. It was sparingly soluble in cold aqueous alkali, but dissolved completely on warming (Found : Hg 55·1 ; C 25·4% ; $C_{10}H_{18}O_8Hg_2$ requires Hg 54·3, C 26·0%).

7-*Hydroxy*-4 : 8 -*dimethyl*-3 : 6-*dibromocoumarin*.—The mercury compound (1·6 g.) was suspended in glacial acetic acid (50 c.c.), and a solution of bromine in acetic acid added with shaking until the colour of bromine persisted. The solid rapidly went into solution as the bromination proceeded and a clear solution was eventually obtained from which a crystalline pale yellow solid deposited slowly. After shaking for about half an hour the mixture was left overnight, poured into ice water (500 c.c.) and the solid filtered off after about 2 hours. It was then macerated with potassium bromide solution to remove mercuric bromide, filtered, washed with water and crystallised repeatedly from glacial acetic acid. The dibromo compound was thus obtained as rectangular rods melting above 300°. (Found : Br 38·8 ; $C_{11}H_8O_3Br_2$, $C_2H_4O_2$ requires Br 39·2%.)

Coupling with Diazocompounds.—The hydroxy-dimethylcoumarin (0·1 g.) was dissolved in excess of glacial acetic acid and the solution divided into two halves. To one of these was added an ice cold solution of diazotised paranitraniline containing sodium acetate. There was no formation of colour or precipitate inmmediately. When enough of the solution of the diazo salt was added to cause a slight turbidity and the mixture left overnight, a deep red solid was deposited by the morning. To the other half water was added to cause slight turbidity. On leaving overnight it formed a small precipitate which was practically colourless thus showing that an azo-dye was formed in the first case as a result of coupling.

7-*Allyloxy*-4 : 8-*dimethylcoumarin*.—The hydroxy-coumarin (0·6 g.) in acetone solution was heated with allylbromide (2 g.) and anhydrous potassium carbonate (2 g.) for 7 hours on a water bath. The solvent was then evaporated, the residue treated with cold water (100 c.c.) and allowed to stand overnight. The solid that had separated was filtered, macerated with cold dilute ammonia in order to remove unchanged hydroxy-coumarin, filtered and washed. On recrystallisation from dilute olcohol the allyl ether was obtained as long thin rectangular plates melting at 108°. (Found : C 72·9, H 6·1 ; $C_{14}H_{14}O_3$, requires C 73·1, H 6·1 %.) Yield was good being 0·6 g.

Claisen rearrangement. 7-*hydroxy*-4 : 8-*dimethyl*-6-*allylcoumarin*.—The allyl ether (0·5 g.) was heated in a test tube at about 220° by means of an oil bath for 2½ hours. Care was taken that at no time the temperature exceeded 230°. After cooling, the mass was extracted with alcohol and filtered. On adding excess of water to the alcoholic solution a pale yellow solid was obtained melting at 150–160° (yield 0·4 g.). Treatment with dilute ammonia did not bring about any improvement. After repeated crystallisation from alcohol it was obtained in the form of star-like clusters of short needles and

rectangular plates melting at 168–70°. (Found : C 73·1, H 6·0 ; $C_{14}H_{14}O_3$ requires C 73·1, H 6·1%.) The substance had a marked tendency to form supersaturated solutions in alcohol from which hard big crystals separated slowly after prolonged standing. If on the other hand water was added to the hot solution until turbidity appeared, almost all the substance came down on cooling.

Summary.

The behaviour of 7-hydroxy-coumarin indicates that there exists a double bond between 7 and 8 positions. But 7-hydroxy-4 : 8-dimethyl-coumarin couples with diazocompounds and undergoes mercuration in the benzene nucleus. Its acetyl derivative undergoes the Fries migration and its allyl ether the Claisen transformation. It is therefore concluded that the nuclear double bonds are not fixed and are capable of assuming alternative positions.

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THE HYDROXYL FREQUENCY IN THE RAMAN SPECTRA OF ACIDS AND ACID SALTS.

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1. Introduction.

In several previous communications by the author, it has been shown from the study of the Raman effect that strong inorganic acids undergo progressive dissociation in aqueous solutions. A typical case is that of nitric acid.[1] In very concentrated solutions of this acid, the Raman lines attributed to the undissociated molecule, HNO_3, are the most prominent and the lines due to the product of dissociation, NO_3 ion, are very weak. As the concentration falls, the HNO_3 lines decrease and the NO_3 lines increase in intensity. A similar effect due to dilution has been observed on the Raman spectra of iodic, sulphuric, selenic, selenious, phosphoric,[2] and arsenic[3] acids and are explained as due to successive and continuously increasing ionisation of the acid molecules.

Recently, Martin and his collaborators[4] have studied the Raman effect in a large number of strong electrolytes with a view to discover any line characteristic of the cation-anion oscillations and determine their degree of dissociation in concentrated solutions. These authors found, in agreement with the conclusions of the earlier workers, that no line is present in those electrolytes, which could be definetely attributed to the cation-anion binding. In the case of 100 per cent. sulphuric acid and chloroacetic acid they were unable to record any band characteristic of the O–H group and therefrom they were led to conclude that these acids are completely ionised even in the concentrated solutions and the anomalous variation in the number and the intensity of the Raman lines in them with dilution has to be attributed

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[1] Ramakrishna Rao, I., *Proc., Roy, Soc.*, (**A**), 1930, **127**, 279; Woodward, L. A., *Phy. Zeit* 1931, **32**, 690.

[2] Venkateswaran, C. S., *Proc. Ind. Acad. Sci.*, (**A**), 1935, **2**, 119; 1936, **3**, 25, 307 and 533.

[3] Fehrer, F., and Morgenstern, G., *Zeit. f. Anorg. u. Allg. Chem.*, 1937, **232**, 169.

[4] Bernstein, H. J., Romans, R. G., Howden, O. H., and Martin, W. H., *Trans. Roy. Soc.*, Canada, 1936, **30**, 49.

not to progressive dissociation but to the various degrees of hydration of the ions or to the existence of other molecular forms in solution.

Further, in a recent contribution to the study of the structure of the acids of phosphorus, Simons and Fehrer[5] have also failed to record the O–H frequency in the phosphoric, phosphorus and hypophosphorus acids and they have concluded that these acids exist in the true acid form and not as pseudo-acids[6] possessing hydroxyl groups.

The present investigation* was undertaken in order to decide whether the hydroxyl frequency exists or not in inorganic acids. The results have also been discussed in relation to the so-called ' hydrogen bond ' in these compounds.

2. *Experimental.*

Since the frequency due to the O–H group falls almost in the same region as the Raman bands of water, it is important that for the purpose of this investigation, the substances examined should be in the anhydrous condition. Among the substances studied, sulphuric acid was in 100 per cent. liquid state, free from water and thrice distilled in vacuum. The crystals of iodic, selenious and telluric acids and sodium dihydrogen phosphate and potassium bisulphate were dried in a desiccator and examined in an air-tight tube. The crystals were investigated by the method of complementary filters devised by Ananthakrishnan,[7] which yields a remarkably clear region between 4358 and 4916 Å., where these bands appear. In the case of liquid sulphuric acid only one filter was used in the path of the incident light to cut off the 4358 radiations of the source. The times of exposure ranged from 3 to 6 days.

3. *Results.*

All compounds studied have yielded a broad and weak band at about 2900 to 3400 cm.$^{-1}$ The frequency shifts and the breadth of this band are given in Table I. The other vibration frequencies in these substances† are not included, since they do not come into consideration in the present investigation. The last column in the table gives the difference between the frequency shift of the centre of the band and the free hydroxyl frequency, 3608 cm.$^{-1}$, as observed in potassium hydroxide.

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[5] Simons, A., and Fehrer, F., *Zeit. f. Anorg. u. Allg. Chem.*, 1936, **230**, 289.

[6] Hantzsch, *Ber.*, 1925, **58**, 941.

* A preliminary note on the results of this investigation was published in *Nature*, 1937, **140**, 151.

[7] Ananthakrishnan, R., *Proc. Ind. Acad. Sci.*, (**A**), 1937, **5**, 76.

† Solid selenious acid has yielded a new weak line at 2217 cm.$^{-1}$, which has to be attributed to Se-H oscillations. (*Vide* C. S. Venkateswaran, *Proc. Ind. Acad. Sci.*, (**A**), 1936, **3**, 533.)

TABLE I.

Exciting line 4046·5 Å.

Substance	Raman band of O–H in cm.$^{-1}$			Deviation from normal
	Beginning	Middle	End	
H_2SO_4 100% liquid	2794	2985	3172	623
HIO_3 crystals	2834	2979	3125	629
H_2SeO_3 ,,	2973	3057	3141	551
H_6TeO_6* ,,	2985	3121	3257	487
NaH_2PO_4 ,,		3460 ±20		148
$KHSO_4$,,	2750	to	3800	

* Telluric acid solution has yielded three vibration lines with frequency shifts 647 (10), 624 (1) and 357 (4), of which 647 is highly polarised and the other two are depolarised.

The following characteristic features of the bands may be noted:— (1) The O–H frequency in these acids and acid salts is represented by a band which is weak, broad and diffuse as compared with the other vibration frequencies in their spectra. (2) The magnitude of the frequency shift of this band is considerably lower than the O–H frequency in potassium hydroxide. It is also distinctly lower than the well-known bands of water at 3205, 3420 and 3580 cm.$^{-1}$, and therefore there is no possibility of confusing with the latter. (3) There is a progressive fall in the frequency shift and a diminution of the intensity and increase in diffuseness of the band as the strength of the acid increases. (4) In the case of sulphuric acid the band appears to be resolved into two components. (5) The O–H band in NaH_2PO_4 is weak, but comparatively narrow and has a greater shift. In $KHSO_4$ the band appears only as a weak, diffuse darkening extending from 2750 to 3800 cm.$^{-1}$

4. *Discussion of Results.*

1. *In relation to electrolytic dissociation and molecular structure.*—According to Martin and his collaborators,[4] if the oxyacids exist in the unionised state in the concentrated aqueous solutions, the dissociation of the molecules takes place about the O–H bond and hence the obvious method of investigation of the degree of dissociation by the Raman effect is to follow the changes in the intensity of the band due to the hydroxyl group. In a second

communication[8] they have also arrived at the result that the frequency characteristic of the O–H group in compounds containing that group has a fairly constant value of about 3500 cm.$^{-1}$ Both of these conclusions require modification. The results given in Table I show that in all the acids studied, the weak and diffuse band appearing at about 3000 cm.$^{-1}$ could be assigned only to the hydroxyl group in them. A similar band reported in the literature for a number of other acids is given in Table II. While the existence

TABLE II.

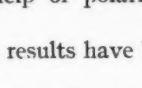
Acid	Frequency shift in cm.$^{-1}$			Deviation from normal	References
	Beginning	Middle	End		
HNO_3		3070		538	W. H. M.
H_3PO_4	2700	3360	3700	248	Méd.
H_3AsO_4	3060	3470	3670	138	F. and M.
H_3BO_3	3172	3256		352	R. A.
HCOOH		3350		258	L. B.

W. H. M. = Martin, W. H., and others, *loc. cit.*; Méd = Médard, *Compt. Rend.*, 1934, **198**, 1407; F. and M. = Fehrer and Morgenstern, *loc. cit.*; R. A. = Ananthakrishnan, R., *Proc. Ind. Acad. Sci.*, (A), 1937, **5**, 200; and L. B. = *Landolt-Bornstein Tabellen*, Weiler.

of this band in all these acids proves the presence of the hydroxyl group, their low intensity does not permit of even qualitative measurements of the study of progressive dissociation with increasing dilution. The extreme feebleness of these bands cannot be explained as due to the presence of only a few undissociated molecules in the pure state, but has to be attributed to the same cause as the diffuseness and the lowering of the frequency of these bands.

From the presence of the OH band in the acids cited in Tables I and II, we are led to conclude that they exist in the form of pseudo-acids. This conclusion is further justified by the fact that in concentrated solutions of these acids, a greater number of Raman lines has been recorded than is to be expected if the molecules were in the true acid form. Thus for the nitric acid the true acid form, (HNO_3), should yield only three lines similar to the NO_3 ion, but in fact, six lines have been recorded which could be

[8] Bernstein, H. J., Romans, R. G., Howden, O. H., and Martin, W. H., *Trans. Roy. Soc.*, Canada, 1936, **49**, 37.

assigned, with the help of polarisation data,[9] to a pyramidal molecule  · Similar results have been obtained for the other acids as well. The failure to record the O–H band in the acids of phosphorus by Simons and others is probably due to the heavy background present in their spectra. The results of Fehrér and Morgenstern with arsenic acid, however, which is homologous to phosphoric acid in all its properties, are in agreement with the pseudo-form of the acid molecule.

2. *In relation to the 'hydrogen bond'.*—The presence of the band characteristic of the O–H group in the acids and the acid salts referred to in Tables I and II is also significant from the point of view of the so-called hydrogen bond put forward by Latimer and Rodebush.[10] By hydrogen bond is meant a chemical linkage in which a hydrogen atom usually belonging to a hydroxyl or amino group causes an intermolecular association of two or more molecules or an intramolecular binding (chelate ring) in a single molecule whenever the configuration is favourable. Thus, the association of molecules of the general type ROH is explained as due to the formation of an incipient bond as follows : R–O–H – – · Pauling[11] is of opinion that whenever a hydrogen bond is formed during association or chelation, the hydrogen involved in the linkage no longer remains attached to a particular oxygen atom, but is in a state in which it is equally shared by the two oxygen or electronegative atoms. In such cases, the electronegative atoms are brought nearer to each other. The hydrogen atom will be in a state of resonance between the two and no definite O–H bond will be established.

The experimental evidence in support of the existence of the hydrogen bond in hydroxy compounds is furnished by the crystal structure data which indicate that in such compounds the oxygen-oxygen distance has an extremely low value of 2·55 Å., while double the radius of the ion O^{--} is 2·70 Å. and of the neutral oxygen is 3·9 Å. Hilbert, Wulf, Hendricks and Liddel[12] have shown that the hydroxyl group involved in a hydrogen bond does not yield the infra-red absorption characteristic of the group and suggested that the absence of this band may be taken as a criterion for the

[9] Venkateswaran, C. S., *Proc. Ind. Acad. Sci.*, (A), 1936, **4**, 174.

[10] Latimer, W. M., and Rodebush, W. H., *J. Amer. Chem. Soc.*, 1920, **42**, 1419.

[11] Pauling, L., *ibid.*, 1936, **58**, 94.

[12] Hilbert, G. E., Wulf, O. R., Hendricks, S. R., and Liddel, U., *Nature*, 1935, **135**, 147.

formation of the hydrogen bond. Recent investigations in the infra-red absorption by Errera and Mollet,[13] Buswell, Dietz and Rodebush,[14] Fox and Martin,[15] and Badger and Bauer[16] have shown, however, that in a number of cases in which the hydroxyl group is known to be linked by a hydrogen bond, the narrow band at 2·769 μ characteristic of the free O–H does not disappear completely as Wulf and his co-workers thought, but appears as a broad, intense band at a longer wave-length of about 3 μ. The change in the wave-length is attributed by them to a weakening of the O–H bond. These investigations in the infra-red are mostly confined to organic compounds and the simultaneous presence of certain C–H frequencies in the above region is a great handicap for the exact determination of the position of the shifted band.

All the substances included in the present investigation possess one or more hydroxyl groups and are known to contain the hydrogen bond. They are also free from C–H group and any shift in the region of 3000 cm.$^{-1}$ has to be assigned only to O–H oscillations. The results given in Table I give for the first time the characteristic features of the Raman band of the hydroxyl group involved in a hydrogen bond. The following conclusions may be made :—

1. There is a definite Raman spectrum for the hydroxyl groups in compounds which possess hydrogen bond.

2. The frequency of this band is considerably lower than the free hydroxyl frequency. The magnitude of lowering is a maximum in sulphuric acid and gets smaller as the strength of the acid diminishes. In dihydrogen sodium phosphate the frequency shift is of the same order as in alcohols.

3. The breadth of the band is greater the more the lowering in the frequency shifts. The diffuseness of these bands is in agreement with the results of the infra-red absorption.

4. Though the band characteristic of the hydrogen bond is intense in the infra-red absorption, it is very weak in Raman scattering. It is not possible from the present investigation to obtain any idea about the relative intensities of this band in different compounds.

An approximate estimate of the change in the energy caused in the O–H linkage due to the formation of the hydrogen bond is made by Fox and Martin and they have shown that in phenol and alcohols in which the

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[13] Errera, J., and Mollet, P., *Nature*, 1936, **138**, 882.

[14] Buswell, A. M., Dietz, V., and Rodebush, W. H., *J. Chem. Phys.*, 1937, **5**, 501.

[15] Fox, J. J., and Martin, A. E., *Proc. Roy. Soc.*, (A), 1937, **162**, 419.

[16] Badger, R. M., and Bauer, S. H., *J. Chem. Phys.*, 1937, **5**, 839 and 852.

band appears at a frequency of 150 to 300 cm.$^{-1}$ lower than the free O–H band, the energy involved will be between 3000 and 6000 cal./mol. Following their method of calculation, this change in the energy is a maximum in sulphuric acid and will be about 12,500 cal./mol. This is slightly less than $\frac{1}{8}$ of the dissociation energy of the normal O–H bond; but compared to the changes of energy in associated alcohols it is considerable and hence we have to conclude that the hydrogen bond is very strong in it.

TABLE III.

Substance	Frequencies in cm.$^{-1}$	Substance	Frequencies in cm.$^{-1}$
H–O–H vapour	3646 st, 3654 st	$Ba(OH)_2$	3417 vw
„ liquid	3205 m, 3420 st, 3580 w	CH_3OH	3430 (400 cm.$^{-1}$) b broad
„ solid 0° C.	3200 st, 3321 m, b	C_2H_5OH	3240 m, b, 3359 st, b
„ „ −190° C.	3090 st, 3135 w	C_3H_7OH	3400 b
H_2O_2	3395 m, b	C_4H_9OH	3400 b
NaOH	3630 st	glycol	3250 to 3550
KOH	3608 st	glycerin	3450
$Sr(OH)_2$	3484 w	Phenol	3500

Note *st* = strong, *m* = medium intensity, *w* = weak, *vw* = very weak and *b* = broad.

In Table III the available data[17] on the O–H Raman frequency in a few hydroxides and alcohols are recorded. It may be seen that while the alkali hydroxides give the maximum frequency shift of about 3600 cm.$^{-1}$, there is a distinct lowering of frequency in the other compounds. The diminution of frequency is, however, much less than in the case of the strong acids given in Tables I and II. As in acids, this lowering of the O–H frequency in these cases has to be attributed to the formation of inter- or intra-molecular linkage involving the formation of a hydrogen bond. On the basis of this conception, we have to postulate that the water molecules

[17] For references see *Landolt-Bornstein Tabellen*, Weiler.

are unassociated in the vapour state ; but in the liquid and solid states they are associated through hydrogen bonds, the strength of this bond increasing with decrease of temperature.

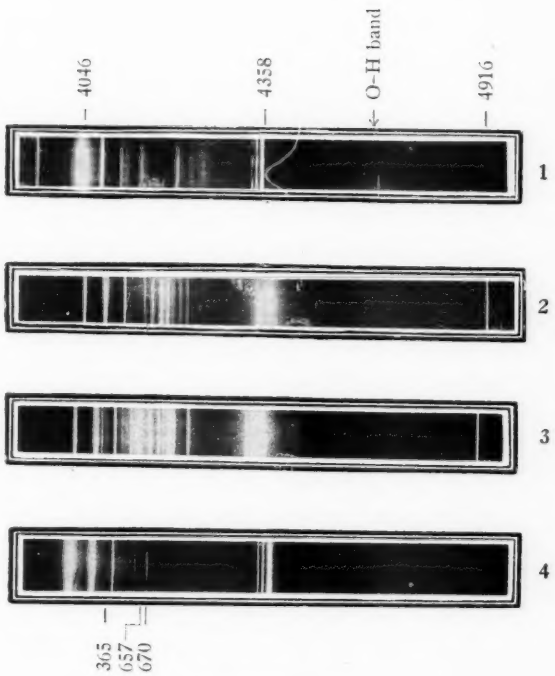
According to Bernal and Megaw,[18] a distinction should be made between hydrogen bond and hydroxyl bond. In the hydrogen bond, the hydrogen atom is in a state of oscillation between two oxygen atoms and there is no definite OH group and the O–O distance is reduced to 2·55 Å. In the hydroxyl bond, the hydrogen atom remains attached to one oxygen atom, but is at the same time linked to another electronegative atom, which tends to weaken the O–H bond and the O–O distance is greater than 2·7 Å. It appears to the author that this distinction between the two kinds of bonds is artificial. If the results in Tables I, II and III are taken together, it will be seen that the change in the hydroxyl frequency is graded and in no case has it completely disappeared. We have to conclude from this that an incipient chemical linkage called ' hydrogen bond ' is formed in all these compounds causing association between two or more molecules or chelation in single molecule, the strength of the linkage alone varying from compound to compound. The hydroxyl group preserves its identity in all cases ; but its bond strength is diminished in a manner proportionate to the strength of the hydrogen bond. The diffuseness and the extreme weakness of the Raman band due to the hydrogen bond, however, requires explanation.

In conclusion, the author wishes to express his respectful thanks to Sir C. V. Raman for his kind interest in the work.

Summary.

The Raman spectra of sulphuric, iodic, selenious and telluric acids and sodium dihydrogen phosphate and potassium bisulphate have been obtained under long exposure and using complementary filters. In every case, a band characteristic of the O–H group has been recorded. The band is weak and diffuse and is shifted to a frequency considerably lower than that due to free hydroxyl group. The results are discussed in relation to electrolytic dissociation and molecular structure of these compounds. From the nature of the spectra, the characteristic features of the Raman band due to the so-called hydrogen bond are deduced. Some new Raman frequencies in selenious and telluric acids are indicated in the paper.

[18] Bernal, J. D., and Megaw, H. D., *Proc. Roy. Soc.*, (**A**), 1935, **151**, 384.



The Raman Spectra.

1. H_2SO_4. 2. HIO_3. 3. H_2SeO_3. 4. H_6TeO_6.

THE RECIPROCITY THEOREM IN COLLOID OPTICS AND ITS GENERALISATION.

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1. The Case of Transverse Scattering.

It is well known that the light transversely scattered by any colloidal solution is, in general, only partially polarised. The imperfectness of polarisation arises from two causes, (1) the scattering particles being of finite size not small compared with the wave-length of light and (2) the scattering particles being anisometric in shape and/or anisotropic in structure. In order to separate these two effects, the depolarisation of the Tyndall scattering should be measured with the incident light (1) unpolarised, (2) polarised with vibrations perpendicular to the plane containing the incident and scattered beams and (3) polarised with vibrations parallel to this plane. The values, both relative and absolute, of the three quantities ρ_u, ρ_v and ρ_h thus measured, are determined by the size, shape and structure of the colloidal particles and their distribution in space. The value of ρ_v mainly depends on the lack of spherical symmetry in shape or structure of the particles, while the value of ρ_h is specially sensitive to the size of the particles and to their grouping in space. The author[1] has shown that there is a very general relation connecting the three quantities ρ_u, ρ_v and ρ_h namely

$$\rho_u = (1 + 1/\rho_h)/(1 + 1/\rho_v) \qquad (1)$$

which is valid for any colloidal solution irrespective of the size, shape, structure and distribution of the particles contained in them and also for light of any wave-length.[2] This relation can be derived theoretically by considering an unpolarised beam of light passing horizontally through the solution; this may be regarded as made up of two beams of equal intensity and unrelated in phase, one with vibrations vertical and the other with vibrations horizontal. The light scattered transversely in the horizontal direction by an element of volume of the solution can therefore be supposed to

[1] R. S. Krishnan, *Proc. Ind. Acad. Sci.*, (A), 1935, **1**, 717 and 782.

[2] ————, *ibid.*, 1935, **1**, 915 ; 1935, **2**, 221 ; 1936, **3**, 211 ; 1937, **5**, 94, 305, 407, 498, 551 and 577 ; *Curr. Sci.*, 1937, **6**, 90.

be made up of four components V_v, H_v, V_h and H_h, the first two arising from the vertical component and the last two arising from the horizontal component of the incident beam. The depolarisation factors ρ_u, ρ_v and ρ_h are then given by

$$\rho_u = (H_v + H_h)/(V_v + V_h) \; ; \; \rho_v = \frac{H_v}{V_v} ; \quad \rho_h = \frac{V_h}{H_h}. \tag{2}$$

According to the theories of Rayleigh and Mie, the two quantities H_v and V_h both vanish when the particles are spherical in shape and isotropic in structure. Hence, when they are present they have a common origin, namely, the anisotropy of structure and/or the non-spherical shape of the particles. Further, H_v and V_h are obviously related to each other in a reciprocal fashion, the direction of electric oscillation in the incident and the scattered radiations in them being interchanged. Hence we may write

$$H_v = V_h. \tag{3}$$

Relation (1) follows directly on combining (2) and (3).

The principle of the experimental method employed to test relation (3) consists in splitting the incident unpolarised light by means of a double-image prism into two beams of equal intensity, but polarised in the vertical and horizontal planes respectively. The light scattered transversely in the horizontal direction is also viewed through another double-image prism which is so orientated that the images given by it are separated in a vertical plane. Four images of the tracks corresponding to the components V_v, H_v, V_h and H_h will then be visible at the same time and their intensities may be compared. Typical photographs are reproduced in Plate II. In all the cases studied, it is found that the two middle components, *i.e.*, H_v and V_h, are always exactly identical in intensity and colour, establishing thereby the validity of relation (3) and therefore also of relation (1). The colour and intensity of the two outermost components differ greatly from each other and from those of the middle two components, and these differences furnish indications regarding the size and shape of the scattering particles.

For the most general case of the scattering by particles of arbitrary size, shape or structure the equality of the components H_v and V_h can be derived from theoretical considerations by applying the "*Principle of Reciprocity*" as indicated below.

Let a beam of plane polarised light of intensity I with vibrations vertical be incident along the X-axis of a system of co-ordinates X, Y, Z on the colloidal particles placed at O. Let the X-Y plane be the horizontal plane, the transverse observation being made along the Y-axis. This will give rise to a vertical component V_v and a horizontal component H_v in the light

scattered along OY [full lines in Fig. 1 (*a*)]. In the same way a horizontal electric vector of intensity I incident on the particle along the X-axis gives

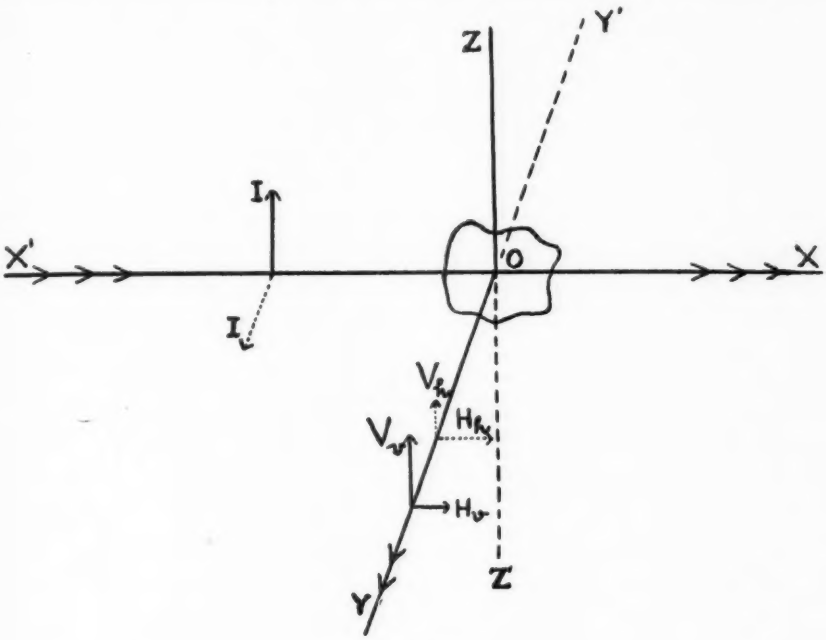


FIG. 1 (*a*)

rise to a vertical component V_h and a horizontal component H_h in the light scattered along the Y-axis [dotted lines in Fig. 1 (*a*)]. The depolarisation factors ρ_u, ρ_v and ρ_h of the solution are given by

$$\rho_u = \frac{\Sigma H_v + \Sigma H_h}{\Sigma V_v + \Sigma V_h}; \quad \rho_v = \frac{\Sigma H_v}{\Sigma V_v}; \quad \rho_h = \frac{\Sigma V_h}{\Sigma H_h}. \tag{4}$$

Σ indicates that the summation should be extended for all the particles in a volume element of the colloidal solution.

Imagine the direction of observation and the direction of the incident beam interchanged keeping the particle under observation fixed in position and orientation [see Fig. 1 (*b*)]. We may now find the state of polarisation in the scattered light by applying the "*Theorem of Reciprocity*" stated by the late Lord Rayleigh[3] in the following words :—"*A force of any type acting alone produces a displacement of a second type equal to the displacement of the*

[3] Lord Rayleigh, L., *Theory of Sound*, 1926, **1**, 93.

first type due to the action of an equal force of the second type." The vertical electric force I in the incident beam along the X-axis produces a vertical displacement V_v in the scattered beam along the Y-axis [Fig. 1 (*a*)]. Hence, by the reciprocity principle, a vertical force in the incident beam along the Y-axis [Fig. 1 (*b*)] must produce a vertical displacement V_v in the scattered beam along the X-axis. Then again if a horizontal force I in the incident beam along the X-axis produces a vertical displacement V_h in the scattered beam along the Y-axis [see Fig. 1 (*a*)], we infer from the reciprocity principle that a vertical force I in a beam incident along the Y-axis must produce a horizontal displacement V_h in the scattered beam along the X-axis [see Fig. 1 (*b*)]. Similarly, it follows that a horizontal force I in the incident beam

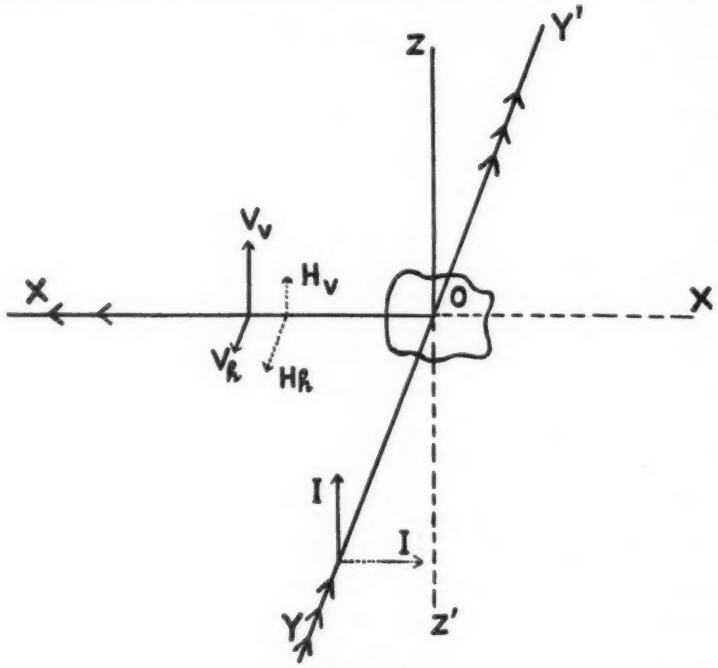


FIG. 1 (*b*).

along the Y-axis would give rise to a vertical displacement H_v and a horizontal displacement H_h in the scattered beam along the X-axis. In the case represented in Fig. 1 (*b*) the depolarisation factors ρ_u', ρ_v' and ρ_h' would then be given by

$$\rho_u' = \frac{\Sigma V_h + \Sigma H_h}{\Sigma V_v + \Sigma H_v}; \quad \rho_v' = \frac{\Sigma V_h}{\Sigma V_v}; \quad \rho_h' = \frac{\Sigma H_v}{\Sigma H_h}. \tag{5}$$

But, now, we may remark that

$$\rho_u = \rho_u' ; \quad \rho_v = \rho_v' \text{ and } \rho_h = \rho_h' \tag{6}$$

provided the particles in the colloidal solution considered in the aggregate have no preferred orientation in the horizontal plane XY. For, in such a case, the depolarisation factors should not depend on the actual direction of observation and the actual direction of the incident beam, so long as these two directions lie in the same horizontal plane and are at right angles to each other. On comparing (4) and (5), we see that if relations (6) are to subsist, we must have

$$\Sigma \, \mathrm{H}_v = \Sigma \, \mathrm{V}_h \tag{7}$$

It is important to notice that H_v and V_h for an individual particle of arbitrary size and shape orientated in a specific way, are not equal to each other. Actually, from the expressions given by Rayleigh[4] for the case of small ellipsoidal particles, it is seen that H_v and V_h are not equal for one such particle for a fixed orientation in space. But if an averaging be carried out over all orientations of the particle in the horizontal plane which are similarly situated with respect to a vertical axis, it is easily verified from the expressions given by Rayleigh that the two quantities mentioned above become identical. Thus it is clear that the reciprocity relations embodied in (1) and (3) are valid, not for a single colloidal non-spherical particle, but only for a solution containing a large number of particles which have no preferred orientation in the plane of observation. By combining (4) and (7) we get relation (1) which will hold good for the transverse scattering of light by a colloidal solution irrespective of the size, shape, structure and distribution of particles provided, however, they have no preferred orientation in the plane containing the incident and the scattered beams.

2. *The Case of Oblique Scattering.*

We may now proceed to generalise the reciprocal theorem (1) for oblique directions of scattering. In the most general case of large anisometric and anisotropic particles, the quantities $\overline{\mathrm{V}}_v$, $\overline{\mathrm{H}}_v$, $\overline{\mathrm{V}}_h$ and $\overline{\mathrm{H}}_h$ are finite and their values depend on the angle of scattering γ. Hence the depolarisation factors ρ_u, ρ_v and ρ_h of the light scattered in a direction OR in the horizontal plane by an element of volume of the colloidal solution, will markedly be functions of γ. But if the particles in that volume element have no preferred orientation in the plane of observation, the depolarisation factors measured in any particular direction in the same plane will only depend on the angle of scattering γ and not on the actual direction of observation and that of the incident beam. Hence, applying the same reasoning as in the preceding

[4] Lord Rayleigh, I., *Phil. Mag.*, 1918, **35**, 373.

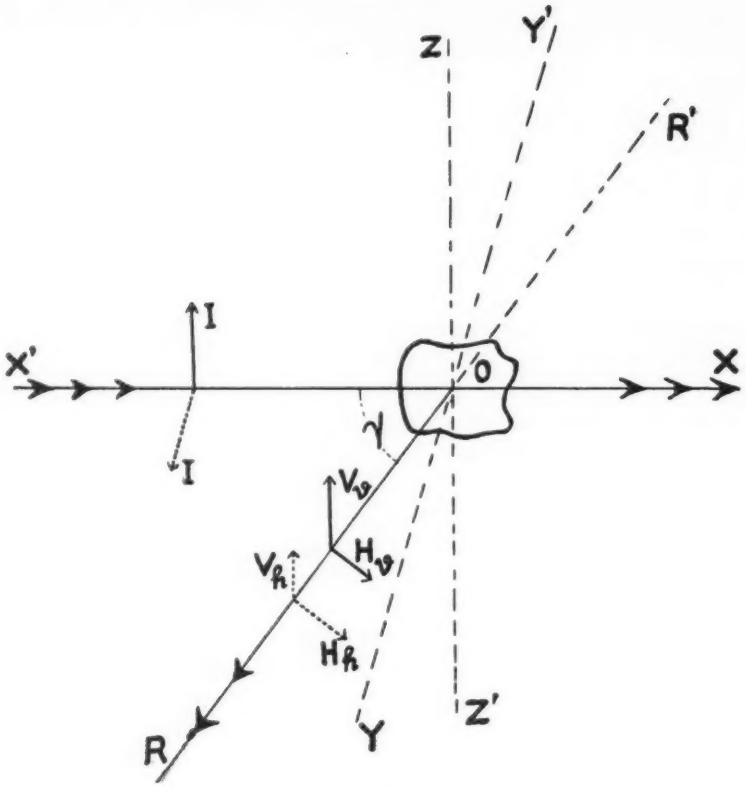


FIG. 2 (*a*).

section, we see that relations (4), (5), (6) and (7), and consequently the reciprocity relation (1) should hold good for any direction of observation OR in the horizontal plane [see Figs. 2 (*a*) and 2 (*b*)], although the actual values of the quantities involved are different for different directions. In general, the evaluation of the four quantities $\bar{V}_v$, $\bar{H}_v$, $\bar{V}_h$ and $\bar{H}_h$ and hence ρ_u, ρ_v and ρ_h for any value of γ is difficult. But from symmetry considerations it can be seen that if the particles are randomly orientated in space, $\bar{V}_v$ will be equal to $\bar{H}_h$ for $\gamma = 0°$ and 180°. Hence ρ_v and ρ_h will be equal and ρ_u will attain the value of unity for these values of γ. In certain simple cases, the directional dependence of the three quantities ρ_u, ρ_v and ρ_h can be calculated from the theories of Rayleigh[5] and Mie.[6]

[5] Lord Rayleigh, I., *loc. cit.* ; *Scientific Papers*, **5**, 547.

[6] G. Mie, *Ann. d. Phys.*, 1908, **25**, 377.

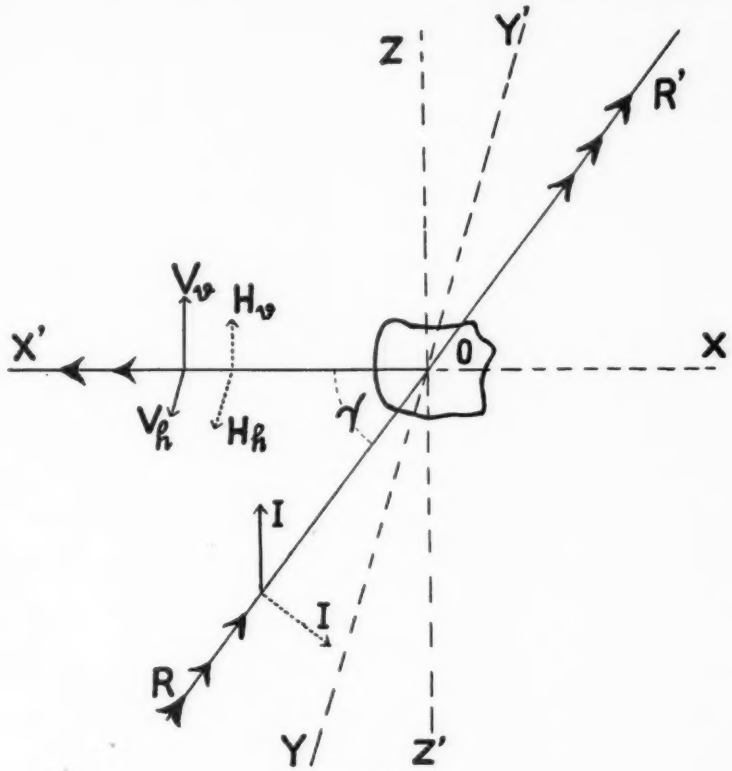


FIG. 2 (*b*).

CASE 1. *Small spherical particles.*—For particles of size small compared with the wave-length of light, the components H_v and V_h are both equal to zero not only for the transverse direction but also for any direction in the horizontal plane. Hence, it follows that ρ_v and ρ_h are both equal to zero for all values of γ. The component V_v will be independent of the angle of scattering. The intensity of the component H_h depends on the direction of observation. For any oblique direction its value is given by

$$H_h = V_v \cos^2 \gamma. \tag{8}$$

Hence $\rho_u = \cos^2 \gamma$ and is zero at 90° and is 1 at 0° and 180°. Its variation is represented graphically in curve (1) in Fig. 3. The curve is symmetrical about the minimum point.

CASE 2. *Large spherical particles.*—In this case also Mie's theory indicates that the two components H_v and V_h both vanish for all values of

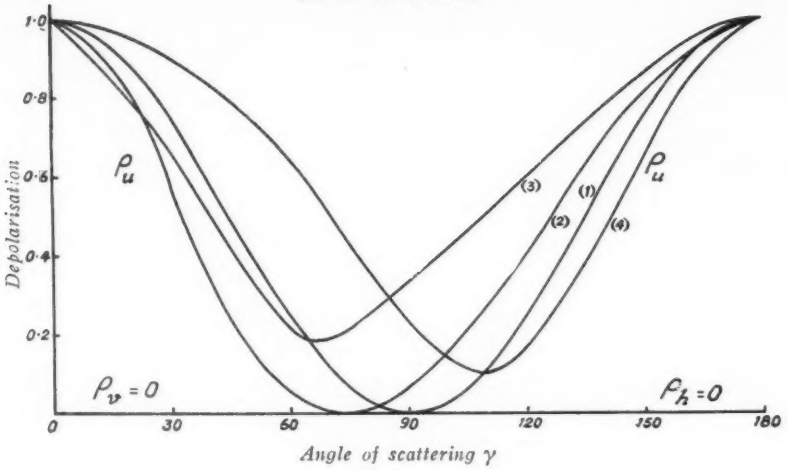


FIG. 3.

Depolarisation as a function of angle of scattering for spherical particles.

1. Particles of radius $r < 10$ A.U.
2. Dielectric particles of radius $r = 100\ \mu\mu$
3. „ „ „ $r = 120\ \mu\mu$
4. Gold spheres of radius $r = 160\ \mu\mu$

γ and hence ρ_v and ρ_h continue to be equal to zero. The components V_v and H_h have finite values for all values of γ, and in consequence when the incident light is unpolarised, the laterally scattered light is partially polarised. The values of ρ_u for spherical particles of moderately small size calculated from Mie's theory, are plotted against the angle of scattering γ in curves (2), (3) and (4) in Fig. 3, from which it will be seen that ρ_u has the value of unity for $\gamma = 0°$ and 180°, and intermediately shows a pronounced minimum. As the size of the particle increases, the minimum is displaced towards the direction of decreasing γ in the case of dielectric spheres, and towards the direction of increasing γ in the case of metallic particles. Further, with increasing particle size the minimum value of ρ_u increases progressively. When the size of the particles exceed a certain value, the curve for ρ_u becomes violently oscillatory. In all these cases ρ_v and ρ_h are zero for all values of γ, and their graphs therefore coincide with the X-axis.

CASE 3. *Small ellipsoidal particles.*—In the case of ellipsoidal particles of size small compared with the wave-length of light and randomly orientated in space, Rayleigh's theory indicates that $\overline{V}_v$, $\overline{H}_v$, $\overline{V}_h$ and $\overline{H}_h$ have finite values and that the two quantities $\overline{H}_v$ and $\overline{V}_h$ are equal for all values of γ. The intensities of the components $\overline{V}_v$, $\overline{H}_v$ and $\overline{V}_h$ do not depend on γ, while

that of $\overline{\mathrm{H}}_h$ is given by

$$\mathrm{H}_h = \overline{\mathrm{V}}_v \cos^2\gamma + \overline{\mathrm{H}}_v \sin^2\gamma. \qquad (9)$$

For this, the values of ρ_u, ρ_v and ρ_h may be readily calculated (see Fig. 4).

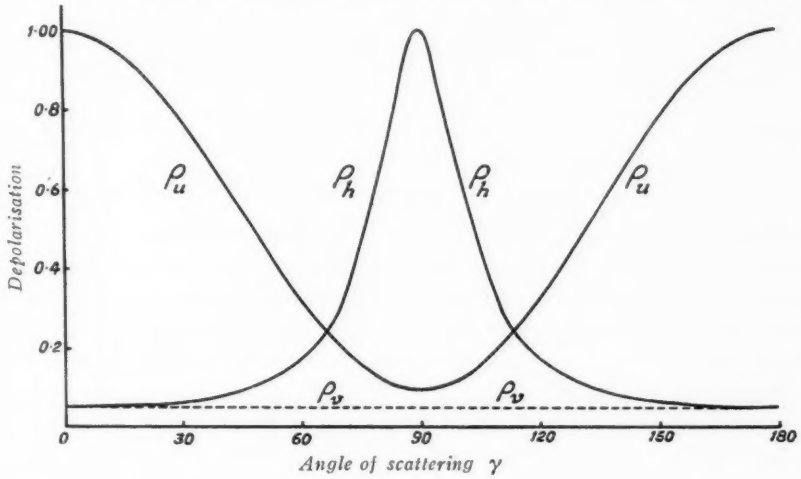


FIG. 4.

Depolarisation as a function of angle of scattering for small ellipsoidal particles.

ρ_v is independent of γ and its graph is therefore a straight line parallel to the axis of X. ρ_u and ρ_h, on the other hand, are markedly functions of γ. The curve of ρ_u shows a minimum equal to $2\rho_v/(1+\rho_v)$ at $\gamma = 90°$, while ρ_h reaches the maximum value of unity at the same angle. For $\gamma = 0°$ and 180°, ρ_v and ρ_h become equal, while ρ_u attains its limiting value of unity.

3. *Experimental Verification.*

The experimental set up for the measurement of the depolarisation factors at various angles of scattering is shown in Fig. 5. The apparatus consisted of a rigid tripod stand to which was fixed a circular disc which was graduated in degrees. A movable arm T was attached to the fixed support, which could be rotated in a horizontal plane about an axis passing through the centre of the graduated disc. Inside the movable arm were fixed a double-image prism D and a square ended nicol N capable of independent rotation, with their axes coinciding with the axis of the tube. The double-image prism was orientated so as to have the vertical and horizontal components of the scattered light separated in a vertical plane.

The light emerging out of the illuminated aperture A (2 mm. square) was passed through a long focus lens of very small aperture. At the focus

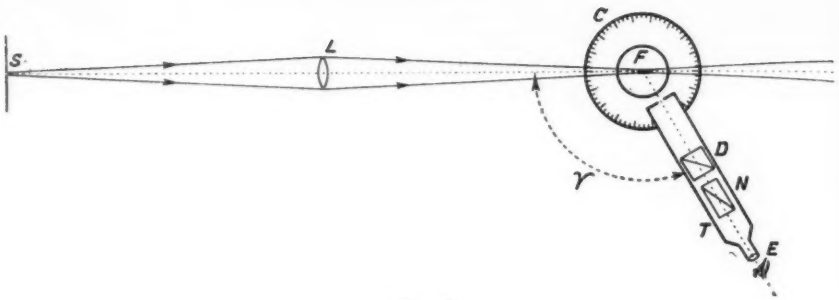


FIG. 5.

the light passed through a transparent fused silica flask placed right at the centre of the disc C. The flask was coated all over the outside with black paint except for a narrow strip 0·75″ wide running along half the circumference of the flask. The scattered light was viewed through a vertical slit attached to the end of the movable arm T, which was nearer to the flask.

Before taking depolarisation measurements, relation (7) was tested out in the following way. A second double-image prism was introduced in the path of the incident beam at a suitable distance from the flask containing the colloidal solution. It was orientated in such a manner that the upper beam was polarised with vibrations vertical. The nicol was removed from the movable arm T and the scattered light was observed through the double-image prism D. Four images of the tracks were seen corresponding to the components $\overline{V}_v$, $\overline{H}_v$, $\overline{V}_h$ and $\overline{H}_h$. The movable arm was set at various inclinations with respect to the incident beam and the relative intensities of the four components in the case of graphite sol and arsenic trisulphide sol were examined visually. For various settings of the arm T, it was found that the two middle components $\overline{H}_v$ and $\overline{V}_h$ were always equal in intensity and colour, establishing thereby the validity of the reciprocity theorem irrespective of the direction of observation in the horizontal plane. It was also found that the intensities of the four components were considerably greater in forward directions than in the backward directions. The effect was very striking in the case of graphite sol in which the particles were coarser than those in the arsenic trisulpdide sol.

The depolarisation factors ρ_u, ρ_v and ρ_h were then measured in the usual way. Measurements were made with white light in the case of the graphite sol whereas in the case of the arsenic trisulphide sol, an orange filter was inserted in the path of the incident beam. The values of ρ_u, ρ_v and ρ_h are given in Tables I and II. The depolarisation factors are plotted against the angle of observation and the curves are reproduced in Figs. 6–9.

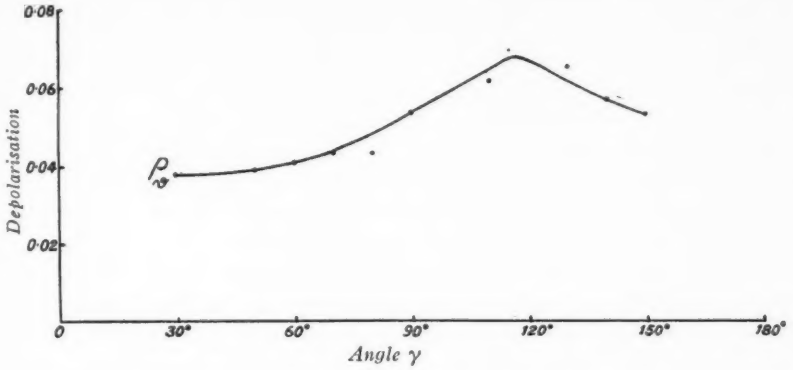


FIG. 6.

Depolarisation (ρ_v) as a function of angle of scattering for graphite sol.

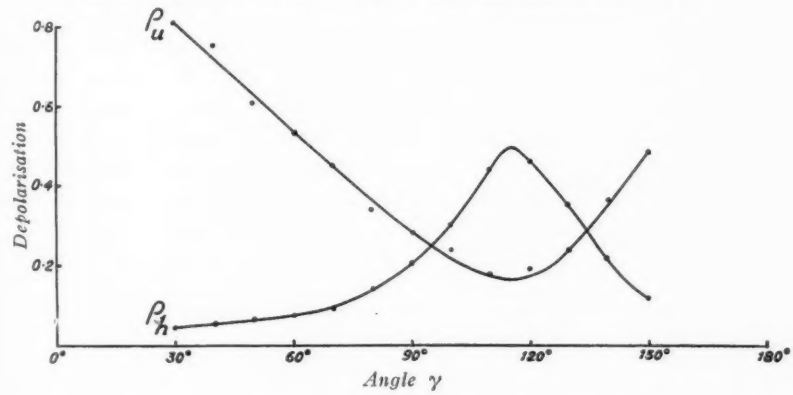


FIG. 7.

Depolarisation (ρ_u and ρ_h) as a function of angle of scattering for graphite sol

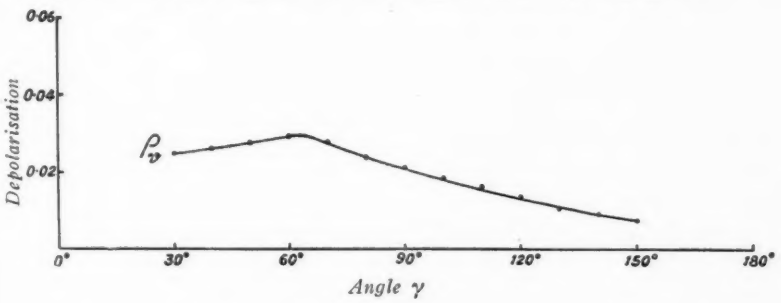


FIG. 8.

Depolarisation (ρ_v) as a function of angle of scattering for arsenic trisulphide sol.

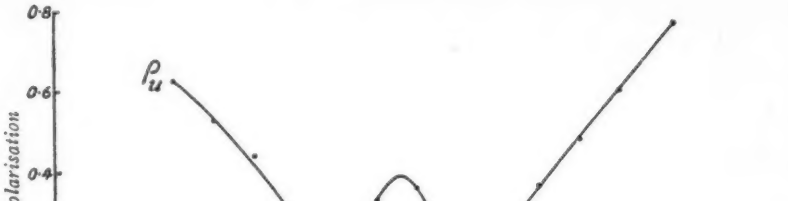


FIG. 9.

Depolarisation (ρ_u and ρ_h) as a function of angle of scattering for arsenic trisulphide sol.

TABLE I.

Depolarisation factors of graphite sol with white light.

γ	30° %	40° %	50° %	60° %	70° %	80° %	90° %	100° %	110° %	120° %	130° %	140° %	150° %
ρ_v ..	3·78	3·78	3·95	4·14	4·33	4·33	5·33	5·99	6·2	6·7	6·57	5·76	5·33
ρ_h ..	4·91	5·43	6·7	7·82	9·6	14·2	20·8	30·1	44·65	46·8	35·73	20	12
ρ_u (obs.)	81	75	61	53·8	45·5	34·3	28	24	18·2	19·8	24·3	33·8	49
ρ_u (cal.)	79·6	67·7	60·5	54·8	39·7	33·4	29·3	24·4	18·9	19·66	23·4	32·6	47·7

TABLE II.

Depolarisation factors of arsenic trisulphide sol with orange filter.

γ	30° %	40° %	50° %	60° %	70° %	80° %	90° %	100° %	110° %	120° %	130° %	140° %	150° %
ρ_v ..	2·4	2·64	2·8	2·95	2·8	2·4	2·16	1·85	1·62	1·4	1·1	0·93	0·77
ρ_h ..	4·14	5·33	6·93	10·7	19·4	33·3	36·1	18	8·77	4·33	2·5	1·72	1·1
ρ_u (obs.)	62·7	53	44·2	28·9	15·9	8·63	7·95	11·5	23·3	36·9	49·0	61·0	81
ρ_u (cal.)	58.9	50.8	42	29.0	16.8	9.6	7.97	11.9	20.	34.8	45.1	58.5	70.0

4. *Discussion of Results.*

The last row in Tables I and II gives the values of ρ_u calculated from the observed values of ρ_v and ρ_h according to relation (1). The fairly satisfactory agreement between the observed and calculated values of ρ_u indicates that the reciprocity theorem is true not only for the transverse horizontal direction but also for any angle of scattering in the horizontal plane. It is instructive to compare the experimental curves of ρ_u, ρ_v and ρ_h given in Figs. 6-9 with the theoretical curves drawn in Figs. 3 and 4 for large spherical particles and for small ellipsoidal particles respectively. The experimental graphs exhibit characteristics which in some respects combine the features exhibited by the theoretical curves in Figs. 3 and 4 and in other respects are intermediate between them. We shall now comment on these features in detail.

Variations of ρ_u.—The value of ρ_u for the two sols examined falls to a finite minimum value at an angle intermediate between 0° and 180°, but this minimum instead of being at 90°, is shifted to an angle $\gamma > 90°$ for graphite sol to an angle $\gamma < 90°$ for arsenic trisulphide sol ; this indicates that graphite particles simulate metallic particles in their behaviour, whereas arsenic trisulphide particles behave like dielectrics. For the two limiting values of γ (*i.e.*, 0° and 180°), the observed value of ρ_u tends to unity, as it is to be expected theoretically for all particles orientated at random irrespective of their size and shape.

Variations of ρ_h.—The value of ρ_h both for graphite sol and for arsenic trisulphide sol shows a maximum for a value of γ intermediate between 0° and 180°. But this maximum instead of being at 90° as in Fig. 4, is shifted towards smaller or larger values of γ in the same way as the minimum of ρ_u. The curve for ρ_h is in fact markedly unsymmetrical in shape. The theoretical values of this maximum is unity for small ellipsoidal particles and zero for large spherical particles. The observed value for the sols studied is intermediate between these extremes, from which it may be inferred that the particles are neither spherically symmetrical nor small in size.

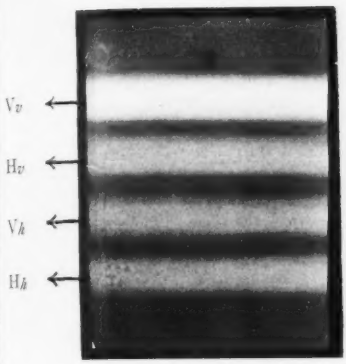
Variations of ρ_v.—Instead of ρ_v being zero as indicated in Fig. 3, or finite and constant in value for all angles of γ as in Fig. 4, the observed ρ_v curves show a maximum for an angle intermediate between 0° and 180°. The curves are distinctly unsymmetrical in shape about the maximum, but both the maximum and the asymmetry are rather less pronounced than in the corresponding curve for ρ_h. In graphite sol the maximum value of ρ_v falls approximately in the same region as the maximum of ρ_h and the

minimum of ρ_u. On the other hand, in arsenic trisulphide sol such a coincidence does not occur; ρ_v is maximum at 60°, whereas ρ_h is maximum at 85°. The experimental curves indicate that both for the values of $\gamma = 0°$ and 180°, the values of ρ_v and ρ_h tend to be equal to each other, as is required by theory. But this common value is not the same when $\gamma = 0°$ and $\gamma = 180°$. For the two cases studied, it would appear that ρ_v at 0° is $>$ or $<$ ρ_v at 180° according as the maximum of the curve of ρ_v is shifted towards 0° or towards 180°.

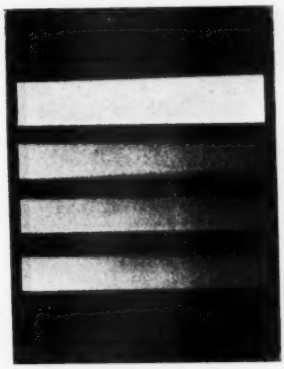
In conclusion, the author wishes to express his grateful thanks to Professor Sir C. V. Raman under whose inspiring guidance the present investigation has been carried out.

5. *Summary.*

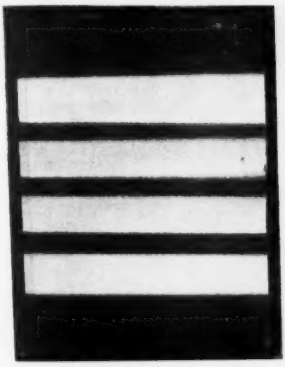
The reciprocity relation $\rho_u = (1 + 1/\rho_h)/(1 + 1/\rho_v)$ connecting the three depolarisation factors ρ_u, ρ_v and ρ_h for the case of the transverse scattering is deduced theoretically. It is pointed out that this relation is valid, not for a single colloidal non-spherical particle with fixed orientation in space, but only for a solution containing a large number of particles which have no preferred orientation in the plane containing the incident and scattered beams. The same considerations are extended to the case of oblique directions of scattering and it is shown that the relation continues to be valid under the same conditions, ρ_u, ρ_v and ρ_h being now functions of the angle γ of scattering and, of course, of the wave-length of the light used. These inferences have been tested out experimentally by the usual double double-image prism method and found valid. Direct measurements of the depolarisation factors ρ_u, ρ_v and ρ_h for oblique scattering for graphite and arsenic trisulphide sols are also found to satisfy the reciprocity relation. Curves representing ρ_u, ρ_v and ρ_h as a function of γ, the angle of scattering, have been plotted and compared with the theoretical curves for the two cases of (*a*) large spherical particles and (*b*) small ellipsoidal particles. The experimental graphs exhibit characteristics which, in some respects, combine the features exhibited by the theoretical curves and in other respects are intermediate between them. The values of ρ_v and ρ_h for the two sols examined show a maximum and the value of ρ_u shows a minimum for a value of γ intermediate between 0° and 180°. The curves for ρ_u, ρ_v and ρ_h are markedly unsymmetrical in shape; but both the maximum and the asymmetry of the curve for ρ_v are rather less pronounced than the corresponding curves for ρ_h and ρ_u.



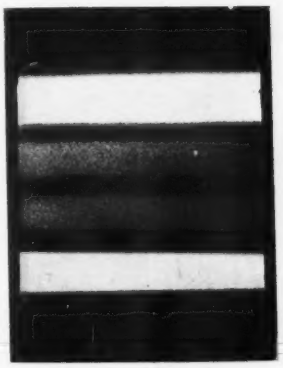
1. Benzene.



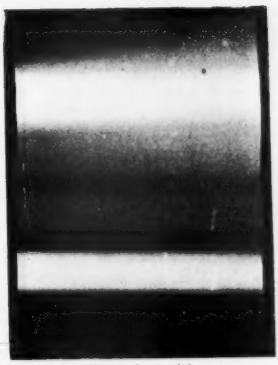
2. Red gold sol.



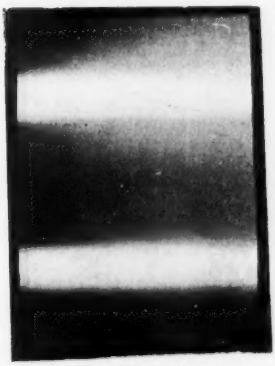
3. Bredig's silver sol.



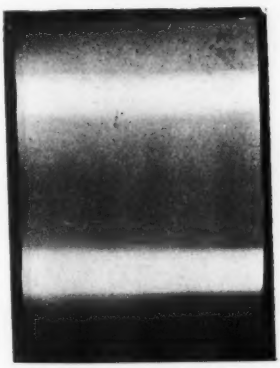
4. Graphite sol.



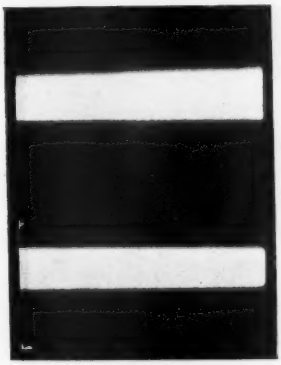
5. Stearic acid sol.



6. Dilute milk.



7. Sulphur suspensions.



8. Dilute toluene emulsion.

9. Concentrated toluene emulsion.

LIGHT-SCATTERING AND OTHER ALLIED PHYSICAL PROPERTIES OF ORDINARY AND HEAVY WATER.

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and
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(From the Department of Physics, Andhra University, Waltair.)

Received December 20, 1937.

1. *Introduction.*

About 50 grms. of heavy water is used in these experiments. It is supplied by the Norsk Hydro-Elektrisk Kvælst ofaktieselskab, marked 99·2 per cent. pure and density $d_4^{20} = 1 \cdot 1049$. The refractive index as measured by us on an Abbe Refractometer at 30° C. is 1·3278 which may be compared with 1·3276 given by Luten.[1] The liquids have been thoroughly purified by repeated distillation in evacuated and sealed double bulbs.

2. *Experimental.*

Compressibilities of H_2O and D_2O.—The compressibilities of both heavy and oridnary water have been measured at the laboratory temperature with a piezometer similar to that designed by Tyrer[2] and recently employed by Dakshinamurti.[3] The adiabatic compressibilities so obtained have been corrected for the compressibility of the glass of the piezometer. The isothermal compressibilities are then derived by making use of the well-known thermodynamic relation

$$\beta_T = \beta_\phi + \frac{T\left(\frac{\partial V}{\partial T}\right)^2 \times 1 \cdot 013 \times 10^6}{J\, V C_p}$$

where β_T and β_ϕ are respectively the isothermal and adiabatic compressibilities, V the specific volume and C_p the specific heat at constant pressure. In the above calculation, the specific volume, its rate of variation and the specific heat for the two liquids are taken from the existing literature.

Measurement of Depolarisation.—The liquids after being repeatedly distilled in vacuum are contained in small bulbs which are immersed in a rectangular glass cell filled with water. Sunlight is focussed into the

[1] *Phys. Rev.*, 1934, **45**, 161.
[2] *Jour. Chem. Soc.* (Lond.), 1914, **105**, 2534.
[3] *Proc. Ind. Acad. Sci.*, 1937, **5**, 385.

bulbs with the help of a high quality photographic lens. The depolarisation is measured visually by the usual Cornu method. The results given here which represent the mean of several observations are corrected for convergence in the incident beam.

Intensity of Transversely Scattered Light.—The intensity of the scattered light has been measured spectroscopically by photographing the tracks in the two liquids under identical conditions. Light from a mercury point source lamp is condensed on to the ordinary water bulb by a lens and the light scattered in a perpendicular direction is condensed by another lens on to the slit of a two-prism glass spectrograph. A wide slit is used and λ 4358 has been photographed with a suitable exposure. The bulb is then replaced by that of heavy water without altering anything else and λ 4358 is again recorded on the plate giving the same time of exposure. During the exposures the mercury lamp is run on a battery and the current is kept constant.

Intensity marks are taken on the same plate by the method of varying slit widths and the relative intensities in D_2O and H_2O are obtained by microphotometring the two patches and the intensity marks in the suitable region.

3. *Results.*

Results are given in the last column of the following table. β_T and $\beta\phi$ obtained in the case of H_2O are in good agreement with those reported earlier by Tyrer for this liquid.

Liquid	Temp.	$\beta\phi \times 10^6$	$\frac{\partial v}{\partial T}$	v	C_p	μ_D	$\beta_T \times 10^6$	100ρ	I Cal.	I Obs.
D_2O	29·5	42·0	$0{\cdot}0_3277$*	·9123*	1·003*	1·3278	42·6	6·4	1·8	1·8
H_2O	29·2	45·9	$0{\cdot}0_3304$*	1·00434*	0·9979*	1·3320*	46·6	6·2	2·0	2·0

4. *Discussion of Results.*

The intensity of the transversely scattered light in a liquid is given as

$$I_1 = I_0 \cdot \frac{\pi^2}{2d^2} \cdot \frac{RT\beta_T}{N\lambda^4} (\mu^2 - 1)^2 \frac{6 + 6\rho}{6 + 7\rho}$$

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*1 V. Slott and Philip H. Bigg, *I.C.T.*, **3**, 24.
2 Tyrer, *Jour. Chem. Soc.* Lond., 1914, **105**, 2534.
3 Jaegar and Steinwehr, L. B. Tabellen.
4 Flatow, L. B. Tabellen.
5 Lewis and Macdonald, *Jour. Amer. Chem. Soc.*, 1933, **55**, 3057.
6 R. S. Brown, Barnes and Maass, *Can. Jour. Research* 1935, **13**, section A. 167–169.
7 D. B. Luten, *Phys. Rev.*, 1934, **45**, 161.

where the various symbols have their usual significance. From this we have

$$\frac{I_1}{I_2} = \frac{(\beta_T)_1}{(\beta_T)_2} \cdot \frac{(\mu_1^2 - 1)^2}{(\mu_2^2 - 1)^2} \cdot \frac{6 + 6\rho_1}{6 + 6\rho_2} \cdot \frac{6-7\rho_2}{6-7\rho_1}. \quad (3)$$

The value given in the table under column 10 for D_2O has been calculated from the above equation assigning an arbitrary value 2 for H_2O. This is in good agreement with the value observed on the same basis and given in the last column.

It may also be noted that the adiabatic and isothermal compressibilities in each of the cases are nearly the same and the ratio of specific heats for heavy water is therefore very nearly unity as in the case of ordinary water.

5. *Summary.*

With a view to compare the intensities of the transversely scattered light in ordinary and heavy water, the adiabatic compressibility and depolarisation have been measured at the laboratory temperature. The isothermal compressibility is calculated with the help of the thermodynamic relation and the figures show that the relative scattering powers of D_2O and H_2O should be as 1·8 : 2. This is in good agreement with the ratio obtained experimentally by photographing the tracks of the transversely scattered light using the λ 4358 radiation from a mercury point source lamp. Ratio of β_T to β_ϕ in heavy water is very nearly unity as in the case of ordinary water.

MAGNETIC ANISOTROPY OF NATURALLY OCCURRING SUBSTANCES.

III. Wood and Its Constituents.

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Received December 9, 1937.

(Communicated by Sir C. V. Raman, Kt., F.R.S., N.L.)

Introduction.

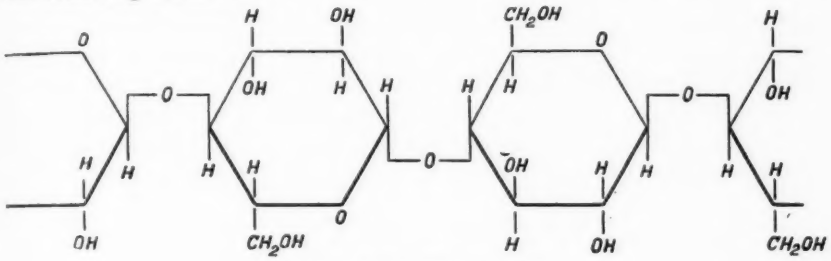
In previous communications[1] the author has shown how the study of the magnetic anisotropy of polycrystalline natural substances like mother of pearl enables us to obtain valuable information regarding the arrangement and orientation of anisotropic crystallites in the aggregate. In the light of the knowledge that we already possess concerning its structure and constitution, an extension of the magnetic studies to the case of wood should be expected to give results of considerable interest. Moreover, a knowledge of the magnetic properties of a universal substance like cellulose is still lacking although many of its other physical properties such as double-refraction, fluorescence, specific heat, hygroscopicity, thermal conductivity, elasticity, etc., have been investigated in greater or less detail. Wood cellulose, in view of the fact that it can be isolated from wood without serious damage to its intrinsic structure, is particularly suitable for the study of magnetic anisotropy. In the present paper the author has studied the absolute diamagnetic susceptibility and anisotropy of wood and its major constituents, with a view to gain additional information regarding their structure and to find out their directional magnetic properties.

The Structure and Constitution of Wood.

A knowledge of the structure of wood and its chemical constitution is essential for the interpretation of the magnetic data. The relevant facts are briefly mentioned in the following pages (for details see *Chemistry of Cellulose and Wood*, Schorger ; *Chemistry of Wood*, Hawley and Wise).[2]

The major constituents of wood are cellulose, lignin and the hemicelluloses. It is now known that cellulose is an ortho-glucosan, *i.e.*, glucose

anhydride. Its empirical formula is $(C_6H_{10}O_5)_n$. The molecule is made up of a chain of glucose residues linked by primary valence forces according to the following scheme :



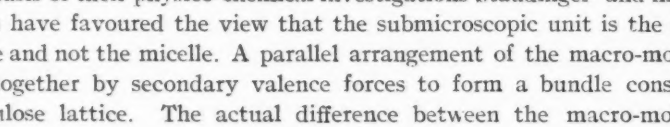
Fragment of Cellulose Chain.

FIG. 1.

Actually the unit in the cellulose chain is the cellobiose residue as will be seen from the arrangement of the glucose residues in the chain. It has been shown that all plant celluloses regardless of their source are identical. The cellulose in wood is found in the cell-wall of the tracheid and is 'crystalline'. With the fibre axis placed perpendicular to a beam of monochromatic X-rays, wood gives a fibre pattern characteristic of cellulose. An examination of teakwood by X-rays has been made by the author[3] and reported in a previous communication in which details regarding the character of the patterns and the information they yield about the structure of wood cellulose are given. The ' crystal structure ' of plant cellulose has been the subject of extensive investigations by Polanyi, Herzog, Sponsler and Dore, Astbury, Andress, Meyer and Mark, E. Sauter, Meyer and Misch and several others.[4] There is still considerable difference of opinion as regards the dimensions of the unit cell and atomic positions, and further investigation will be necessary to settle the question. But there is general agreement regarding the parallel orientation of the long chain molecules more or less in the direction of the fibre axis. Without laying special emphasis in the present uncertain character of the X-ray analysis, on the cell dimensions or the atomic parameters, we can definitely say that the length of the cellulose chain is parallel to the *b* axes of the 'crystallites' which possess monoclinic symmetry and are arranged spirally on the cell-wall (the spirals being steep enough to be almost straight in fibres like ramie and comparatively flat in cotton, wood, etc.) with the *b* axes orientated more or less along the spiral.

The character of the submicroscopic crystalline elements in cellulose is still in the course of being elucidated. Meyer and Mark at first came to the

conclusion from a critical examination of the available X-ray data that these were discrete micelles of dimensions 600 × 50 A. approximately. But it was shown later on that X-ray analysis can give no decisive answer to the question. On the basis of their physico-chemical investigations Staudinger[5] and his collaborators have favoured the view that the submicroscopic unit is the macro-molecule and not the micelle. A parallel arrangement of the macro-molecules bound together by secondary valence forces to form a bundle constitutes the cellulose lattice. The actual difference between the macro-molecular and the micellar schemes is brought out in the figure shown below.



Molecular Lattice. Macro-molecular Lattice.

FIG. 2.

But neither the macro-molecular nor the micellar theory has been able to account for the various physical and physico-chemical properties of cellulose satisfactorily. Recently, Frey-Wyssling, E. Sauter, Kratky and Mark and others[6] have attempted to arrive at a more rational hypothesis. Without entering into a detailed discussion of the various theories it may be said that the following incorporating the ideas of Frey-Wyssling and others is a fairly satisfactory picture of the internal architecture of the cell-wall in cellulose fibres. In the first place, we have the fibrils, running more or less along the fibre axis, which can be made visible under the microscope.[7] These consist of a parallel arrangement of the long-chain molecules of cellulose so placed that there are localised regions of perfect orientation (Kratky and Mark, 1937) which may be said to correspond to the crystalline micelles of the old theory, the forces between the molecules being of the Van der Vaals type in these regions. The dimensions of these micellar regions may be variable over a wide range, sometimes comprising the whole fibril. These ' crystallised ' regions are interspaced by either air cavities or by cementing matter like the pectins and the hemicelluloses. *The important fact to be noticed is that the regularity of arrangement of the cellulose chains in the fibre with their lengths parallel to the fibre axis should give rise to magnetic anisotropy if the individual molecules are themselves anisotropic and* vice versa, *the study of the magnetic anisotropy of wood cellulose should lead to a knowledge of the directional magnetic properties of the cellulose molecule.*

Lignin is present mostly in the primary layer of the cell-wall of the wood fibre known as the middle lamella. The constitution and the morphology of lignin have been the subjects of extensive investigations.[8] Examination by physical methods like microscopy, X-ray analysis and polarisation optics suggest that lignin is amorphous in structure. Various hypotheses have been put forward regarding the manner of combination of cellulose and lignin. One view is that they are chemically combined with each other, but the idea that lignin is adsorbed on cellulose seems to be more plausible in the light of the investigations by the physical methods mentioned above.

The hemi-celluloses[9] are the anhydrides of hexose and pentose sugars ; xylan, araban, mannan and galactan give on hydrolysis xylose, arabinose, mannose and galactose respectively. Not much is known concerning their physical structure and manner of combination with cellulose and lignin.

Experimental Details.

The experiments were all confined to teakwood, the structure of which had been previously examined by the author by X-ray analysis. The wood specimens were subject to extractions with various solvents and subsequent chemical treatment in order to isolate the major constituents. The X-ray analysis was made incidentally to discover whether any radical structural changes had occurred during the extractions, etc. It was found that specimens taken from the less compact layers were subject to changes while those from the most compact layers were practically unaffected. The anisotropy measurements were therefore made on specimens obtained from the most compact dark brown layer of the annual rings. The specimens were prepared for examination as described below :

(1) *Raw wood.*—Washed clean with 5 per cent. HCl and warm water to remove surface impurities, and dried at 102–04° C. for 6 hours.

(2) Extracted with alcohol-benzene for 24 hours and then boiling water for 6 hours and finally dried for 12 hours at 102–04° C.

(3) Wood extracted as in (2) was treated with 5 per cent. NaOH in the cold for 48 hours. Washed several times with dilute acetic acid and then warm water and finally dried for 12 hours at 102–04° C.

(4) Treated with 72 per cent. sulphuric acid in the usual way for 36 hours to obtain lignin which retained the shape and continuous structure of the original sample of wood.

(5) Wood after extraction with alcohol-benzene was chlorinated by the Cross and Bevan method to obtain wood cellulose. The apparatus employed was similar to the one used by Sieber and Walter with a few minor modifications. The procedure described by Dore[10] was adopted with all the necessary precautions. Particular care was taken to see that the samples did not get distorted in shape during chlorination. The prepared samples were also subjected to X-ray analysis. Two samples of wood cellulose were prepared one by partial and the other by complete chlorination. The specimens were dried in the oven for 12 hours at 102–04° C.

(6) Wood cellulose was treated with 17·5 per cent. NaOH in order to get α-cellulose according to the procedure described by Schorger.[11]

Sampling of wood for magnetic measurements.—The wood samples were taken in the form of shavings about 0·5 mm. thick from which pieces 5 × 3 mm. were cut out for the anisotropy measurements. For measurements of absolute susceptibility the samples were taken in the form of powder.

Proximate Analysis of Wood.

The wood samples prepared as described before were all analysed for the determination of their cellulose and lignin contents. The hemi-celluloses and the rest were only indirectly estimated.

It must be stated beforehand that of all the various methods which have been suggested for the determination of the major constituents and groupings in wood, there is scarcely one which can be said to be entirely satisfactory. This, no doubt, is due to the inherent difficulties involved in dealing with a highly complicated substance like wood. The older methods for the determinations of cellulose, lignin and the hemi-celluloses have been continually refined, modified and standardised. However, for purposes of the magnetic investigation a high order of accuracy in analysis is not necessary, especially in view of the fact that the samples have to be taken in the form of shavings about 0·5 mm. thick for the anisotropy measurements, whereas the standard procedure in wood analysis is to start with saw-dust which passes through 80 but not 100 mesh. Therefore, the recent refinements and improvements in the estimation of lignin, etc., have not been adopted. The analytical procedure is outlined below and the results should be sufficiently accurate for interpreting the magnetic data.

Lignin.—The lignin content in the various samples was estimated by treatment with 72 per cent. sulphuric acid in the usual way.[12]

Cellulose.—Cellulose in wood was determined according to the analytical procedure described by Dore and already referred to earlier.

α-Cellulose in wood cellulose was also determined by treatment with cold 17·5 per cent. NaOH as described by Schorger.

Hemi-celluloses.—A direct determination of the hemi-cellulose content was not attempted. These were grouped with the small quantities of the other miscellaneous substances present and the whole indirectly estimated.

Determination of Magnetic Anisotropy.

The anisotropy of wood is comparatively feeble and the technique has to be made specially sensitive. The torsional method described by the author[13] in an earlier communication was employed with the following modifications : (1) Very fine and fairly long (20–30 cm.) quartz fibres were used. (2) The torsional constant of the fibre was determined by suspending at its end a small accurately cut-glass cylinder of known dimensions (3·15 mm. diameter and 4·01 mm. height) with its axis vertical and observing the period of oscillation. (3) A field strength of 7990 gauss was employed, the field being measured in the usual way by means of a calibrated Grassot Fluxmeter and search coil.

The specific anisotropy is given by the formula

$$\chi_1 - \chi_2 = \frac{2\,(\alpha_c - 45)\,\pi.\ c}{180\qquad m\mathrm{H}^2}$$

α_c = The angle through which the torsion head has been rotated ;

m = Mass of the specimen (oven-dry sample) ;

H = Field strength in Gauss ; and

c = Modulus of torsion of the quartz fibre ;

and χ_1, χ_2 are the directions of maximum and minimum susceptibility algebraically in the plane of rotation of the specimen. Only $\chi_{\mathrm{II}^l} - \chi_{\perp^r}$ was found, since, in the case of wood, the anisotropy in the plane of the cross-section of the fibre is negligible in all cases. (χ_{II^l} is the diamagnetic susceptibility along the fibre axis, and $\chi_{\perp^r}$ is that $\perp^r$ to the fibre axis.)

The average dimensions of the specimens employed were 5 × 3 × 0·5 mm.

Absolute Susceptibilities.

The absolute mass susceptibilities were determined by the Curie torsion balance method. The wood samples were all used in the form of fine powder dried at 102–04° C. for 12 hrs. and the susceptibilities compared with that of pure water.

Results.

Raw wood gave somewhat inconsistent values of anisotropy probably due to occluded impurities. After extraction with alcohol-benzene and boiling water consistent values were obtained, the maximum discrepancy noticed being 11 per cent. In all cases at least 10 independent determinations were made and the mean value taken. The results of the magnetic anisotropy measurements are given in Table I. Table II gives the values of absolute susceptibilities and Table III the results of the proximate analysis. A summary of results is given in Table IV.

TABLE I.

Specific Magnetic Anisotropy in C.G.S.—E.M. Units.

Specimen of wood	Mode of suspension	Orientation in the field	Specific magnetic antisotropy $-(\chi_{\parallel} - \chi_{\perp})$, $\times 10^8$
(1) Extracted with alcohol benzene and boiling water	Fibre axis horizontal	Fibre axis perpendicular to the field direction	0·39
(2) After treatment with 5 per cent. NaOH	,,	,,	0·40
(3) Lignin prepared by treatment with 72% sulphuric acid	,,	nil	0·00
(4) (*a*) after partial chlorination,	,,	Fibre axis perpendicular to the field direction	0·68
(*b*) after complete chlorination	,,	,,	0·84
(5) α-Cellulose	,,	,,	0·92

TABLE II.

Absolute Mass Susceptibilities.

(C.G.S.—E.M. Units.)

Wood specimen	$-\chi \times 10^6$
(1) Teakwood : Most compact layer of annual ring	0·44
(2) ,, Least compact layer of annual ring	0·43
(3) ,, After extraction with alcohol-benzene and boiling water	0·47
(4) ,, After treatment with 5 per cent. NaOH ..	0·45
(5) ,, Lignin prepared by treatment with 72 per cent. sulphuric acid	0·42
(6) ,, After partial chlorination	0·48
(7) ,, After complete chlorination : Cross and Bevan cellulose	0·503
(8) ,, α-Cellulose	0·508

The diamagnetic susceptibility of pure double distilled water was taken as $-0{\cdot}720\times10^{-6}$.

TABLE III.

Proximate Analysis of Teakwood.

(Figures refer to percentage of oven-dry specimen taken.)

Specimen	Cellulose %	α-Cellulose %	Lignin %	Remaining hemi-cellulose, etc., indirectly estimated %
(1) Teakwood extracted with alcohol-benzene and water	54·1	39·9	33·5	12·4
(2) Treated with 5 per cent. NaOH	50·9	40·1	44·8	4·3
(3) After partial cholrination	82·8	59·3	14·7	2·5
(4) After complete chlorination : Cross and Bevan cellulose		72·9		

TABLE IV.

Summary of Results.

Wood specimen	Absolute susceptibility $-\chi \times 10^6$	Magnetic anisotropy $-(\chi_{\parallel r}-\chi_{\perp r}), \times 10^8$	Cellulose %	α-Cellulose %	Lignin %	Remaining hemi-celluloses, etc., %	$*\Delta\chi \times 100$ / % of total cellulose $\times 10^8$	$\Delta\chi \times 100$ / % of α-cellulose $\times 10^8$
After extraction with alcohol-benzene and boiling water	0·47	0·39	54	37	33	13	0·72	1·05
After extraction with 5 per cent. NaOH	0·45	0·40	51	40	45	4	0·78	1·00
Lignin prepared by treatment with 72 per cent. sulphuric acid	0·42	..	..	..	100	..	..	..
After partial chlorination	0·48	0·68	83	59	15	2	0·82	1·15
After complete chlorination: Cross and Bevan cellulose	0·503	0·84	100	73	..	..	0·84	1·16
α-Cellulose	0·508	0·92	..	100	..	..	..	0·92

$* \Delta\chi = -(\chi_{\parallel r} - \chi_{\perp r})$.

Discussion of Results.

An examination of Table IV shows that the anisotropy is more or less proportional to the cellulose content of the specimens. It apparently does not depend on the amount of lignin present. α-Cellulose has the maximum specific anisotropy whereas lignin isolated by 72 per cent. sulphuric acid treatment does not show any. The 'crystalline' element responsible for the magnetic anisotropy appears to be cellulose only.

The magnetic measurements, however, do not rule out the possibility of lignin being present as crystallites which are randomly orientated. But X-ray analysis shows that isolated lignin gives only a 'liquid' pattern characteristic of an amorphous substance.[14] There is also nothing indicative of 'crystalline' lignin in the wood patterns obtained. Examination of lignin under the microscope has not revealed any property characteristic of crystals, due to it. Taken together, the X-ray, optical and magnetic investigations lead to the conclusion that lignin in its natural state has an amorphous structure.

Ordinary wood cellulose obtained by chlorination is really a complex substance and consists of what are known as the α, β and γ-celluloses, distinguished from one another by their solubility in 17·5 per cent. NaOH solution. From Table IV we can see that the magnetic anisotropy of wood is essentially due to the α-cellulose in it. It is also seen that treatment with 5 per cent. NaOH which removes a good part of the hemi-celluloses leads to an increase in the value of $\frac{\Delta\chi}{\%\text{ of total cellulose}}$. The initial removal of the hemi-celluloses naturally means a decrease in the total cellulose, for wood cellulose (prepared without pre-treatment with NaOH) contains as much as 20 per cent of the hemi-celluloses. We may conclude from this that the hemi-celluloses like lignin do not contribute to the magnetic anisotropy. In view of their gummy texture it is most probable that they are amorphous in structure.

We also notice that the value of $\frac{\Delta\chi}{\%\text{ of }\alpha\text{-cellulose}}$ is less for α-cellulose than for Cross and Bevan cellulose. This will mean that $\Delta\chi$ is greater for Cross and Bevan cellulose than can be accounted for by the presence of α-cellulose alone in it. The inference is that the β- and γ-celluloses are also anisotropic just like α-cellulose and most probably possess the same 'crystalline' structure.

Magnetic properties of the cellulose molecule.—The diamagnetic anisotropy of cellulose in wood leads to important conclusions regarding the

directional magnetic properties of the cellulose molecule. The diamagnetic susceptibility in the direction of the fibre axis is seen to be maximum. Since the cellulose chains are orientated with their lengths more or less parallel to the fibre axis it follows that the direction of maximum diamagnetic susceptibility is along the chain length. The values of $\chi_{II}{}^{f}$ and $\chi_{\perp}{}^{r}$ can be easily calculated from $\bar{\chi}$ and $\Delta\chi$. We have $\chi_{II}{}^{f} = -0{\cdot}514 \times 10^{-6}$ and $\chi_{\perp}{}^{r} = -0{\cdot}505 \times 10^{-6}$, for α-cellulose.

Now, it is well known from the data of refraction of cellulose[15] that the direction of maximum optical polarisability of the cellulose molecule is also along the length of the chain. The directions of maximum optical polarisability and diamagnetic susceptibility, therefore, coincide. This, in fact, is not surprising since this property is also possessed by long-chain aliphatic compounds like the higher hydrocarbons (C_nH_{2n+2}).[16] By analogy we can also draw the inference that a solution of native cellulose in neutral solvent will exhibit negative magnetic double refraction, in accordance with the orientation theory of Langevin and Born.

My sincere thanks are due to Sir C. V. Raman, Kt., F.R.S., N.L., for his guidance, encouragement and helpful criticism in the course of the work.

Summary.

The diamagnetic anisotropy and absolute susceptibilities of wood, lignin and wood cellulose have been determined. It has been found that the 'crystalline' element in wood is definitely cellulose and that lignin and the hemi-celluloses make no contribution to the magnetic anisotropy, suggesting either a random orientation if they are crystalline or an amorphous structure. In the light of evidence from other sources, it seems most likely that they are amorphous. The anisotropy measurements also indicate that the direction of maximum diamagnetic susceptibility in the cellulose molecule is along the length of the chain. Since it is also known that the direction of maximum electric polarisability too is along the chain length, we find that these directions coincide in the molecule just as in the case of the higher long-chain saturated hydrocarbons.

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THE PHYSICAL IDENTITY OF ENANTIOMERS.

Part V. The Relation between Concentration and Viscosity of Solutions of *d*-, *l*- and *dl*-Forms of Camphor, Iso-nitrosocamphors, Camphorquinone, Camphoric Acid and Sodium Camphorate.

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Received December 1, 1937.

Whereas investigations on the viscosity of solutions of electrolytes have been extremely numerous, those dealing with non-electrolytes are much fewer in number. The most extensively studied example among the non-electrolytes, is perhaps sucrose : Hosking[1] measured the viscosity of solutions containing up to 40 per cent. by weight at temperatures between 0° and 90°, and Bingham and Jackson[2] later made an elaborate study of the viscosity of solutions of this substance.

The viscosity of solutions of stereoisomeric compounds has not been much studied. The observations of Dunstan and Thole[3] on the viscosity of aqueous solutions of optically active and *racemic* tartaric acids, of Thole[4] on several pairs of geometrical isomerides and esters of optically active and *racemic* acids are among the few instances of work of this nature.

The writer[5] has examined the viscosity of solutions of enantiomeric and *racemic* forms of camphor and its derivatives at different concentrations. Two important points emerged from this work : (*a*) the enantiomeric forms had identical values of viscosity ; (*b*) the *racemic* forms had higher viscosity above certain values of concentration, which clearly pointed to the existence of racemate in solution. Since viscosity increases with molecular weight[6] it follows that the racemic substance consists of higher molecular aggregates than the *dextro* and *lævo* isomerides. With increasing dilution, the racemate completely dissociates into the optically active components.

The present paper deals with the problem of finding out a connection between the concentration and viscosity of solutions of the above-mentioned substances.

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[1] *Phil. Mag.*, 1900, **49** (5), 274.
[2] *Scient. Pap. Bur. Stand.*, 1917, No. 298.
[3] *Trans. Chem. Soc.*, 1910, **97**, 1253.
[4] *Loc. cit.*, 1912, **101**, 552 ; 1913, **103**, 25.
[5] *Proc. Ind. Acad. Sci.*, 1937, **5**, 484.
[6] Macleod, *Trans. Farad. Soc.*, 1925, **21**, 158.

The viscosity-concentration graphs of these substances given in the earlier communication[7] did not give straight lines, which indicates that the viscosity of these solutions cannot be expressed by the simple mixture law. Although several formulæ connecting concentration and viscosity have been proposed, the only attempt at rational treatment seems to be that of Einstein[8] who deduced a linear relationship between viscosity and concentration from the fundamental equations of hydrodynamics. The formula of Einstein does not, however, agree with observations, except at very low concentrations. Among the empirical formulæ, which have been proposed, the most useful is that of Arrhenius[9]

$$\eta/\eta_0 = A^C, \quad \text{or } \log \frac{\eta}{\eta_0} = C \log A,$$

in which η is the viscosity of the solution having the concentration C, η_0 that of the pure solvent and A a constant.

The definition of concentration in the above equation is a matter of some difficulty in view of the empirical nature of the relationship. Since, according to Kendall[10] viscosity is essentially the frictional resistance encountered by molecules of a solution in moving over one another, it would seem to be more logical to represent compositions in molecules rather than in weight or volume fractions. Dunstan and Thole[11] found a very good agreement between Green's experimental values of the viscosity of solutions of sucrose[12] and those calculated from Arrhenius' logarithmic formula, when the concentration is expressed in Mols./ 1000 g. of water. This formula fits in well with Bingham and Jackson's data on solutions of sucrose (*loc. cit.*) at 20°, but there is a considerable discrepancy at 0°. In Tables I to VII are given three columns for concentration under C, C′ and C″, in which C, C′ and C″ represent the number of gram-molecules of solute contained in 1000 g. of solvent, 1000 g. of solution and 1000 c.c. of solution respectively. The equation of Arrhenius, $\log \eta/\eta_0 = C \log A$ can be written in the generalised forms, $\log \eta_1/\eta_2 = (C_1 - C_2) \log A$, $\log \eta_1/\eta_n = (C_1 - C_n) \log A$, from which η_0 the viscosity of the solvent is eliminated and in which $\eta_1, \eta_2 \ldots \eta_n$ represent the viscosities of the solution at $C_1, C_2 \ldots C_n$ concentrations. The applicability of this equation to the data given in Tables I to VII can be tested by the constancy of the values of A, A′ or A″. It can also be tested graphically in Figs. 1 to 5 by plotting log η (viscosity of solution) against molecular concentration and seeing if the plots give straight lines.

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[7] *Proc. Ind. Acad. Sci.*, 1937, **5**, 484.
[8] *Ann. d. Phys.*, 1906, **19**, (4), 289.
[9] *Zeit. Physik. Chem.*, 1887, **1**, 285.
[10] *J. Amer. Chem. Soc.*, 1917, **39**, 1790.
[11] *The Viscosity of Liquids*, London, 1914, p. 44.
[12] *Trans. Chem. Soc.*, 1908, **93**, 2033.

Discussion of Results.

(1) *Camphors* (Table I and Fig. 1).—The difference between the extreme values of the constant (A) for the optically active forms is 0·021, that in the values of A′ and A″ being 0·065 and 0·155. It is, therefore, clear that if in the Arrehenius' formula, the concentration is expressed in moles per 1000 g. of the solvent (C), a better agreement is obtained than if the concentration is expressed as moles per 1000 g. of solution (C′), or as moles per 1000 c.c. of solution (C″). The agreement is still better in the case of the

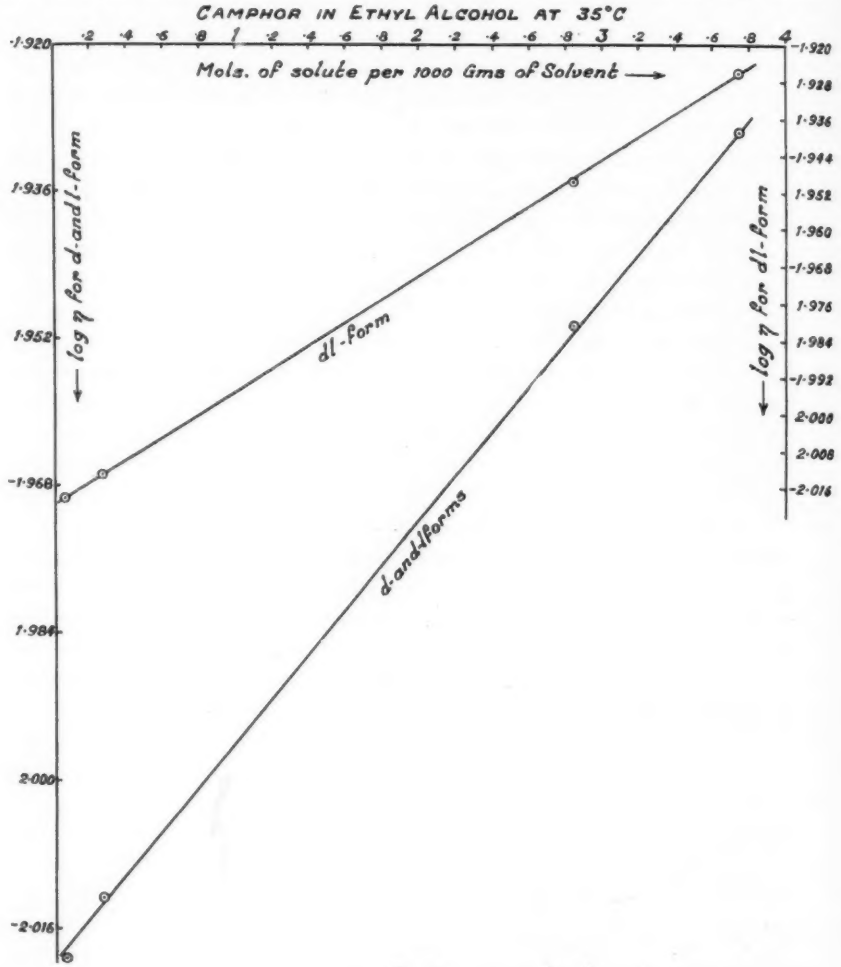

FIG. 1.
Camphor in Ethyl Alcohol at 35° C.

dl-compound, the maximum difference in the values of A being only 0·004. On plotting $\log \eta$ against concentration expressed as C, the graph is a straight line in each case.

(2) *Camphoric Acids* (Table II and Fig. 2).—The values of A in the case of *d*- and *l*-forms show better concordance than those of A′ or A″, the maximum difference, with one exception, being only 0·051, whereas in the other cases the difference becomes 0·53 (A′) and 0·444 (A″). A similar concordance is obtained for the *dl*-isomeride. On plotting $\log \eta$ against C, expressed as above, straight lines are obtained.

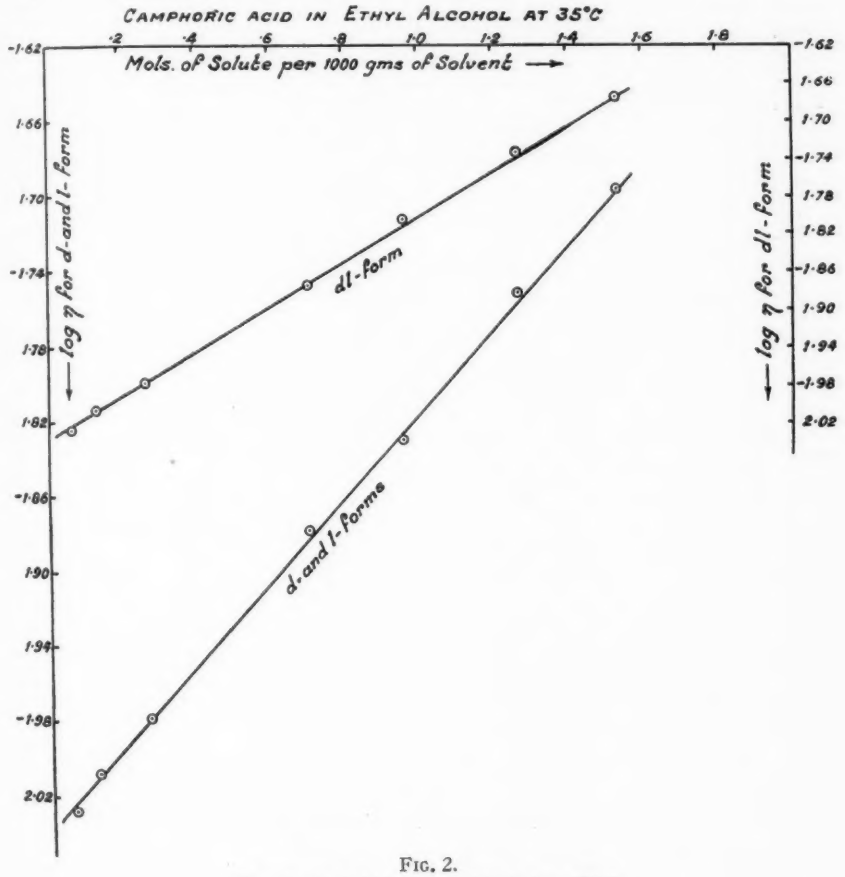
CAMPHORIC ACID IN ETHYL ALCOHOL AT 35°C
Mols. of Solute per 1000 gms of Solvent
log η for d- and l- Form
log η for dl- Form
dl-form
d- and l- forms

FIG. 2.
Camphoric Acid in Ethyl Alcohol at 35° C.

(3) *Sodium Camphorates* (Table III and Fig. 3).—As in the previous two cases, the results of the optically active and *racemic* forms can be expressed

by the Arrhenius' equation, when the concentration is expressed as moles per 1000 g. of solvent. In Fig. 3, the values of log η have been plotted against molecular concentration (C) and in both cases the graph consists of a straight line.

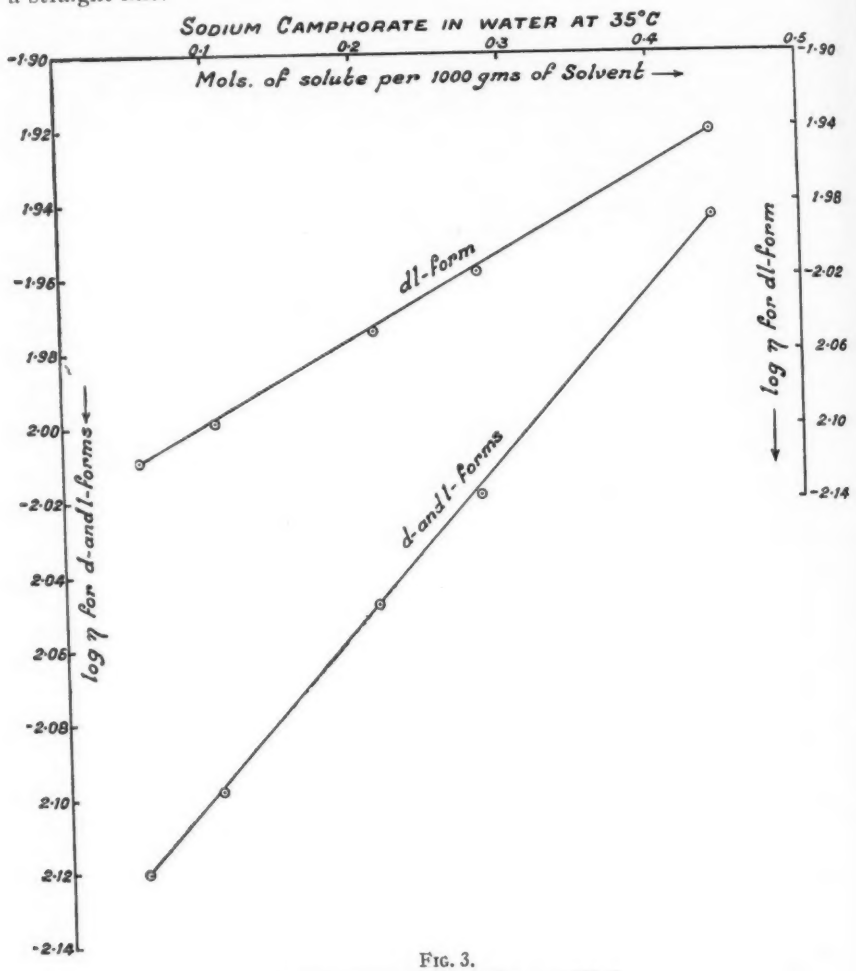

Fig. 3.
Sodium Camphorate in Water at 35° C.

(4) Iso*nitrosocamphors* (Tables IV and V; Fig. 4).—On applying the Arrhenius' formula to the viscosity data for the three forms of the stable and two forms of the unstable *iso*nitrosocamphor, it was found to be inadequate, even if the molecular concentration is expressed in the three different

ways. Accordingly log η-molecular concentration graphs (Fig. 4) are curves and not straight lines. Unlike the previous cases, this system may give non-ideal solutions, as was pointed out by Kendall in the case of certain liquid binary mixtures. The non-ideal solutions in the case of binary mixtures of liquids are distinguished by volume change or heat evolution on mixing the components. The graph of density against composition is a straight line, unless there is any volume change, which will produce a deviation from linearity. The density-composition graph* of *iso*nitrosocamphor departs slightly

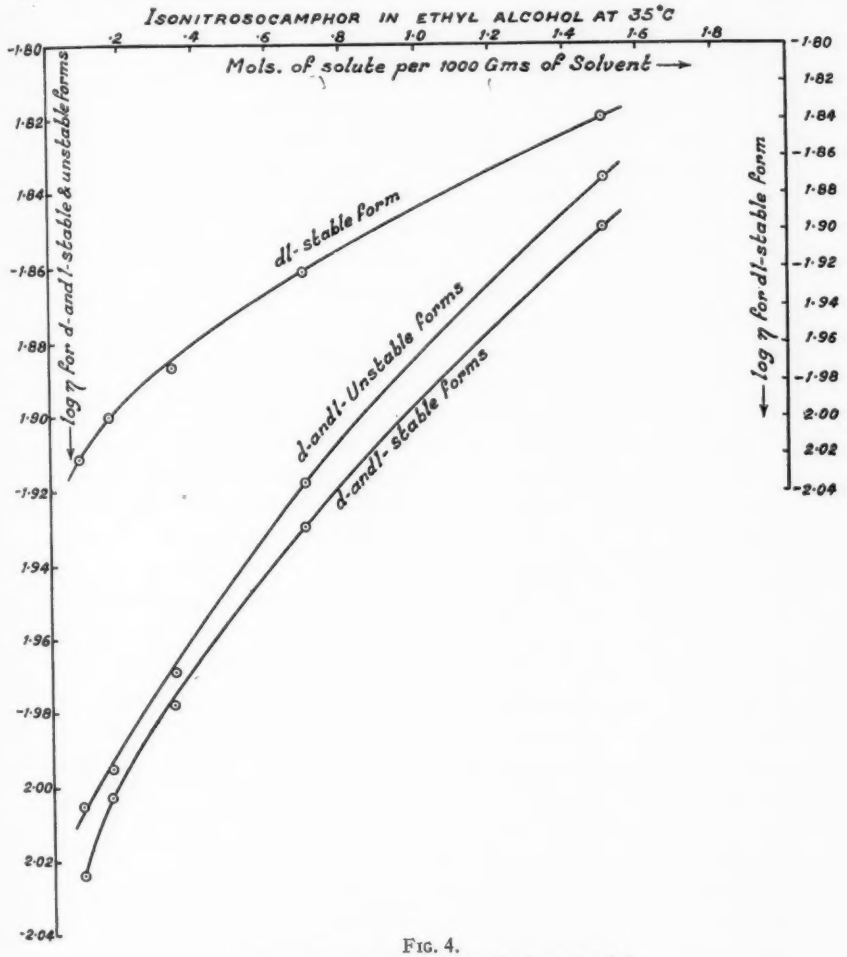
ISONITROSOCAMPHOR IN ETHYL ALCOHOL AT 35°C
Mols. of solute per 1000 Gms of Solvent
log η for d- and l- stable & unstable forms
log η for dl-stable form
dl- stable form
d-and l- Unstable forms
d-and l- stable forms

FIG. 4.
*Iso*nitrosocamphor in Ethyl Alcohol at 35° C.

* This and other density-composition graphs are given in an earlier communication (*Proc. Ind. Acad. Sci.*, 1937, **5**, 484).

from linearity. This fact, coupled with the possible molecular association of the compounds, or the formation of complexes with the solvent, might furnish a clue as to the non-applicability of the Arrhenius' formula. This aspect of the problem requires, therefore, further elucidation.

(5) *Camphorquinones* (Tables VI and VII; Fig. 5).—The remarkable constancy in the value of A for solutions of *d*- and *l*- camphoroquinones in ethyl alcohol (Table VI) shows that the Arrhenius' formula fits in remarkably well. The graph of log η-molecular concentration (C) for these solutions gives a straight line. In conformity with this, the density-composition graph is also a straight line.

The choloroform solutions of the optically active and *dl*-camphorquinone do not fit in with the Arrhenius' formula, when the concentration is expressed as moles per 1000 g. of solvent. It is also interesting to note that the corresponding density-composition graph for these solutions is not linear. If, however, the concentration in the Arrhenius' formula is expressed as moles per 1000 c.c. of solution, the formula holds good and the values of A remain constant and the graph of viscosity-concentration is a straight line (Fig. 5).

Kendall's Cube Root Formula.—Kendall and Monroe[13] in their search for a formula connecting viscosity with composition for ideal solutions, proposed the relation which involves the cube root of the viscosity, namely, $\eta^{\frac{1}{3}} = x\,\eta_1^{\frac{1}{3}} + (1-x)\eta_2^{\frac{1}{3}}$ in which η, η_1 and η_2 are respectively the viscosities of the mixture and of the two components, and x is the molecular percentage of one of them. The formula was found to hold good for solutions of naphthalene and diphenyl in benzene and toluene—where η_2 the "Viscosity" of the solute is unknown—by calculating η_2 from the experimental data. On applying this formula to data given in Tables I- VII, it was found that η_2 the calculated "Viscosity" of the solute, gave generally very variable results. The results of the application of this formula to the optically active isomerides of the substances are given in Table VIII. In four cases, namely, sodium camphorate, camphoric acid, *iso*nitrosocamphor (stable form) and camphor, the calculated value of η_2, the "Viscosity" of the compound, is not a constant. In the case of one system, namely, chloroform solutions of camphorquinone, the value of η_2 is fairly constant. It is however this system for which the density-composition graph is not a straight line and which thus departs from an ideal solution. It is therefore curious that the cube root formula which was held to apply to ideal solutions by Kendall should be applicable to this system. While this agreement is interesting, it is difficult to attach any physical meaning to the value of η_2 (viscosity of "liquid comphorquinone" at 35°; melting point 199°–200°).

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[13] *J. Amer. Chem. Soc.*, 1917, **39**, 1802.

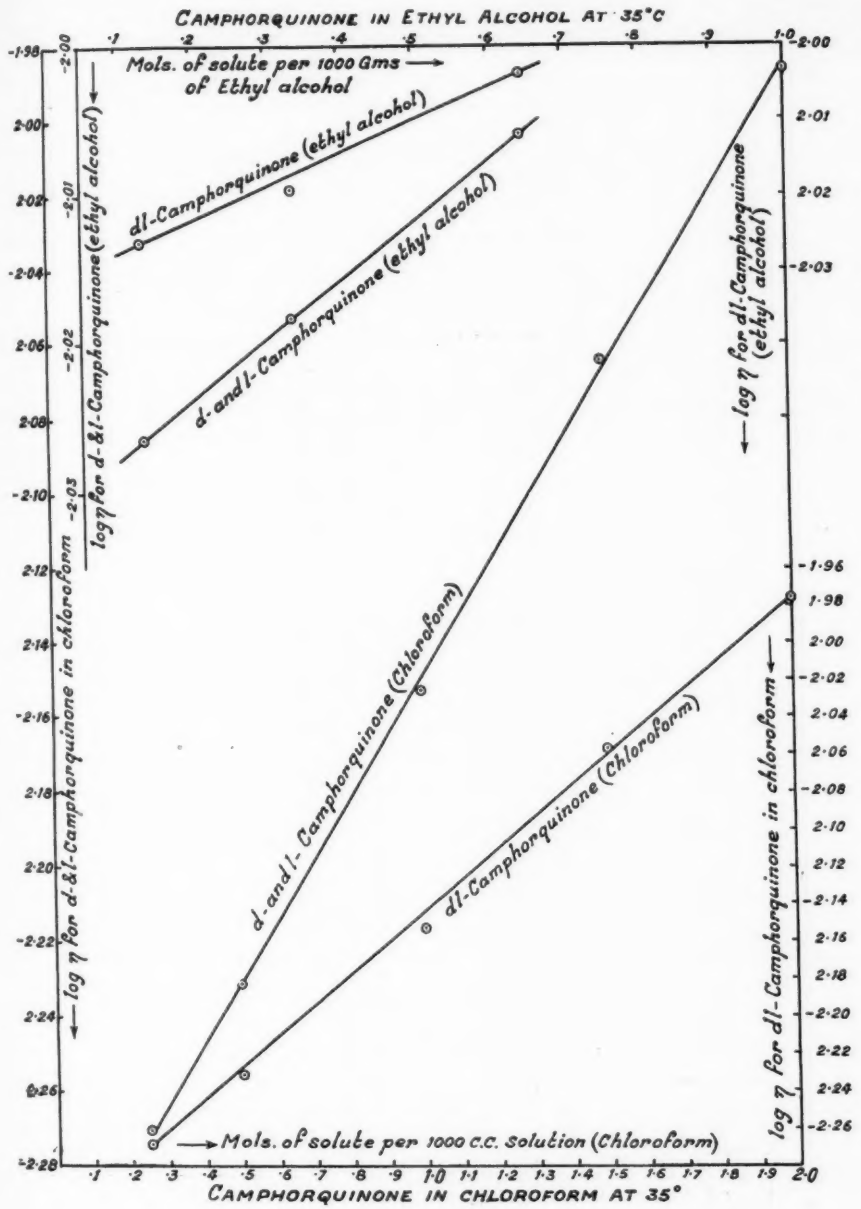
CAMPHORQUINONE IN ETHYL ALCOHOL AT 35°C
Mols. of solute per 1000 Gms of Ethyl alcohol
dl-Camphorquinone (ethyl alcohol)
d- and l-Camphorquinone (ethyl alcohol)
log η for d-&l-Camphorquinone (ethyl alcohol)
log η for dl-Camphorquinone (ethyl alcohol)
d- and l- Camphorquinone (Chloroform)
dl-Camphorquinone (Chloroform)
log η for d-&l-Camphorquinone in chloroform
log η for dl-Camphorquinone in chloroform
Mols. of solute per 1000 c.c. solution (Chloroform)
CAMPHORQUINONE IN CHLOROFORM AT 35°

FIG. 5.

Camphorquinone in Ethyl Alcohol at 35° C.

TABLE I.

Sl. No.	Conc. g./1000 c.c.	Density $[D]^{35°}$	Viscosity (Poise) $[\eta]^{35°}$	log. η	C Mols. of solute per 1000 g. of solvent	A	C′ Mols of solute per 1000 g. of solution	A′	C″ Mols. of solute per 1000 c.c. of solution	A″
				d- and *l*-Camphor. M = 152. Solvent—Ethyl Alcohol.						
1	304·0	0·8370	0·011765	−1·9294	3·7523		2·3895		2·00	
						1·062		1·144		1·165
2	250·0	0·8281	0·011145	−1·9530	2·8451		1·9864		1·645	
						1·054		1·082		1·100
3	30·4	0·7895	0·009712	−2·0127	0·2635		0·2533		0·20	
						1·075		1·079		1·102
4	7·6	0·7859	0·009573	−2·0190	0·0642		0·0636		0·05	
						1·058		1·092		1·111
1	304·0	0·8370	0·011765	−1·9294	3·7523		2·3895		2·00	
				dl-Camphor. M = 152. Solvent— Ethyl Alcohol.						
1	304·0	0·8370	0·011855	−1·9260	3·7523		2·3895		2·00	
						1·062		1·144		1·164
2	250·0	0·8281	0·011236	−1·9495	2·8451		1·9864		1·645	
						1·059		1·088		1·108
3	30·4	0·7895	0·009696	−2·0134	0·2635		0·2533		0·020	
						1·058		1·061		1·078
4	7·6	0·7859	0·009586	−2·0183	0·0642		0·0636		0·05	
						1·059		1·095		1·115
1	304·0	0·8370	0·011855	−1·9260	3·7523		2·3895		2·00	

TABLE II.

TABLE II.

Sl. No.	Conc. g./1000 c.c.	Density $[D]^{35°}$	Viscosity (Poise) $[\eta]^{35°}$	log. η	C Mols. of solute per 1000 g. of solvent	A	C′ Mols. of solute per 1000 g. of solution	A′	C″ Mols. of solute per 1000 c.c. of solution	A″
				d- and *l*-Camphoric Acid. M = 200. Solvent — Ethyl Alcohol.						
1	200·0	0·8513	0·020289	−1·6927	1·535		1·175		1·00	
						1·646		2·257		2·462
2	170·0	0·8425	0·017726	−1·7514	1·264		1·009		0·85	
						1·673		2·154		2·342
3	133·3	0·8275	0·015157	−1·8194	0·960		0·805		0·666	
						1·674		2·014		2·248
4	100·0	0·8155	0·013253	−1·8778	0·699		0·613		0·50	
						1·697		1·888		2·149
5	40·0	0·7935	0·010532	−1·9775	0·265		0·252		0·20	
						1·689		1·754		2·018
6	20·0	0·7860	0·009817	−2·0080	0·131		0·127		0·10	
						1·967		2·032		2·443
7	10·0	0·7811	0·009388	−2·0274	0·065		0·064		0·05	
						1·690		2·001		2·251
1	200·0	0·8513	0·020289	−1·6927	1·535		1·175		1·00	
				dl-Camphoric Acid. M = 200. Solvent —Ethyl Alcohol.						
1	200·0	0·8513	0·021149	−1·6747	1·535		1·175		1·00	
						1·655		2·276		2·485
2	170·0	0·8425	0·018453	−1·7340	1·264		1·009		0·85	
						1·713		2·231		2·446
3	133·3	0·8275	0·015665	−1·8051	0·960		0·805		0·667	
						1·852		2·313		2·621
4	100·0	0·8156	0·013334	−1·8750	0·699		0·613		0·50	
						1·714		1·912		2·181
5	40·0	0·7935	0·010553	−1·9766	0·265		0·252		0·20	
						1·712		1·780		2·056
6	20·0	0·7860	0·009820	−2·0079	0·131		0·127		0·10	
						2·009		2·077		2·512
7	10·0	0·7811	0·009379	−2·0279	0·065		0·064		0·05	
						1·739		2·079		2·354
1	200·0	0·8513	0·021149	−1·6747	1·535		1·175		1·00	

TABLE III.

Sl. No.	Conc. g./1000 c.c.	Density $[D]^{35°}$	Viscosity (Poise) $[\eta]^{35°}$	log. η	C Mols. of solute per 1000 g. of solvent	A	C′ Mols. of solute per 1000 g. of solution	A′	C″ Mols. of solute per 1000 c.c. of solution	A″
d- and *l*-Sodium Camphorate — $C_8H_{14}\begin{matrix}COONa\\COONa\end{matrix}$. $5H_2O$. M = 334. Solvent — Water.										
1	133·6	1·0390	0·011366	−1·9444	0·4418		0·3850		0·400	
						2·941		3·877		3·563
2	88·4	1·0240	0·009575	−2·0189	0·2828		0·2584		0·265	
						2·520		2·962		2·803
3	66·8	1·0170	0·008955	−2·0480	0·2105		0·1967		0·200	
						2·925		3·280		3·177
4	33·4	1·0060	0·007975	−2·0982	0·1028		0·0994		0·100	
						2·737		2·880		2·844
5	16·7	0·9999	0·007570	−2·1209	0·0509		0·0500		0·050	
						2·828		3·363		3·194
1	133·6	1·0390	0·011366	−1·9444	0·4418		0·3850		0·400	
dl-Sodium Camphorate — $C_8H_{14}\begin{matrix}COONa\\COONa\end{matrix}$. $5H_2O$. M = 334.										
1	133·6	1·0389	0·011431	−1·9430	0·4418		0·3850		0·400	
						2·980		3·941		3·618
2	88·4	1·0239	0·009585	−2·0184	0·2828		0·2584		0·265	
						2·625		3·098		2·925
3	66·8	1·0170	0·008939	−2·0487	0·2105		0·1967		0·200	
						2·912		3·265		3·162
4	33·4	1·0062	0·007968	−2·0987	0·1028		0·0994		0·100	
						2·527		2·650		2·618
5	16·7	0·9998	0·007594	−2·1196	0·0509		0·0500		0·050	
						2·830		3·367		3·196
1	133·6	1·0389	0·011431	−1·9430	0·4418		0·3850		0·400	

TABLE IV.

Sl. No.	Conc. g./1000 c.c.	Density $[D]^{35°}$	Viscosity (Poise) $[\eta]^{35°}$	log. η	C Mols. of solute per 1000 g. of solvent	A	C′ Mols. of solute per 1000 g. of solution	A′	C″ Mols. of solute per 1000 c.c. of solution	A″
d- and *l-Iso*nitrosocamphor, stable form, m.p. 153°. M = 181. Solvent—Ethyl Alcohol.										
1	181·0	0·845	0·014146	−1·8494	1·506		1·183		1·00	
						1·254		1·383		1·445
2	90·5	0·813	0·011764	−1·9294	0·692		0·615		0·50	
						1·365		1·448		1·562
3	45·25	0·797	0·010524	−1·9778	0·333		0·314		0·25	
						1·393		1·435		1·570
4	22·625	0·789	0·009948	−2·0023	0·163		0·158		0·125	
						1·808		1·857		2·176
5	11·312	0·786	0·009476	−2·0234	0·081		0·0795		0·0625	
						1·324		1·437		1·533
1	181·0	0·845	0·014146	−1·8494	1·506		1·183		1·00	
*dl-Iso*nitrosocamphor, stable form, m.p. 153°. M = 181. Solvent—Ethyl Alcohol.										
1	181·0	0·845	0·014507	−1·8384	1·506		1·183		1·00	
						1·266		1·402		1·468
2	90·5	0·813	0·011974	−1·9217	0·692		0·615		0·50	
						1·382		1·472		1·592
3	45·25	0·797	0·010660	−1·9722	0·333		0·314		0·25	
						1·459		1·510		1·672
4	22·625	0·789	0·009998	−2·0001	0·163		0·158		0·125	
						1·907		1·963		2·333
5	11·312	0·786	0·009482	−2·0231	0·081		0·0795		0·0625	
						1·348		1·470		1·574
1	181·0	0·845	0·014507	−1·8384	1·506		1·183		1·00	

TABLE V.

Sl. No.	Conc. g./1000 c.c.	Density $[D]^{35°}$	Viscosity (Poise) $[\eta]^{35°}$	log. η	C Mols. of solute per 1000 g. of solvent	A	C′ Mols. of solute per 1000 g. of solution	A′	C″ Mols. of solute per 1000 c.c. of solution	A″
d- and *l*-*Iso*nitrosocamphor, unstable form, m.p. 114°. M = 181. Solvent—Ethyl Alcohol.										
1	181·0	0·845	0·014592	−1·8359	1·506		1·183		1·00	
						1·261		1·394		1·459
2	90·5	0·813	0·012084	−1·9179	0·692		0·615		0·50	
						1·387		1·476		1·598
3	45·25	0·797	0·010743	−1·9688	0·333		0·314		0·25	
						1·420		1·469		1·612
4	22·625	0·7885	0·010126	−1·9947	0·163		0·159		0·125	
						1·320		1·335		1·440
5	11·312	0·785	0·009894	−2·0046	0·081		0·080		0·0625	
						1·313		1·422		1·513
1	181·0	0·845	0·014592	−1·8359	1·506		1·183		1·00	

TABLE VI.

Sl. No.	Conc. g./1000 c.c.	Density $[D]^{35°}$	Viscosity (Poise) $[\eta]^{35}$	log. η .	C Mols. of solute per 1000 g. of solvent	A	C′ Mols. of solute per 1000 g. of solution	A′	C″ Mols. of solute per 1000 c.c. of solution	A″
d- and *l*-Camphorquinone. M = 166. Solvent—Ethyl Alcohol.										
1	77·42	0·8002	0·009865	−2·0059	0·645		0·583		0·466	
						1·095		1·112		1·140
2	41·50	0·7904	0·009591	−2·0182	0·334		0·316		0·250	
						1·098		1·107		1·136
3	16·60	0·7833	0·009408	−2·0265	0·130		0·128		0·100	
						1·096		1·110		1·139
1	77·42	0·8002	0·009865	−2·0059	0·645		0·583		0·466	
dl-Camphorquinone. M = 166. Solvent—Ethyl Alcohol.										
1	77·42	0·8007	0·009920	−2·0035	0·645		0·582		0·466	
						1·124		1·147		1·183
2	41·50	0·7907	0·009564	−2·0193	0·334		0·316		0·250	
						1·209		1·086		1·110
3	16·60	0·7834	0·009417	−2·0261	0·130		0·128		0·100	
						1·106		1·121		1·153
1	77·42	0·8007	0·009920	−2·0035	0·645		0·582		0·466	

TABLE VII.

Sl. No.	Conc. g./1000 c.c.	Density $[D]^{35°}$	Viscosity (Poise) $[\eta]^{35°}$	log. η	C Mols. of solute per 1000 g. of solvent	A	C′ Mols. of solute per 1000 g. of solution	A′	C″ Mols. of solute per 1000 c.c. of solution	A″
				d- and *l*-Camphorquinone. M = 166. Solvent—Chloroform.						
1	332·0	1·330	0·010308	−1·9868	2·004		1·504		2·00	
						1·314		1·561		1·432
2	249·0	1·362	0·008615	−2·0647	1·348		1·101		1·50	
						1·464		1·700		1·503
3	166·0	1·394	0·007028	−2·1532	0·814		0·717		1·00	
						1·505		1·638		1·433
4	83·0	1·420	0·005870	−2·2314	0·374		0·352		0·50	
						1·592		1·665		1·435
5	41·5	1·430	0·005363	−2·2706	0·180		0·175		0·25	
						1·431		1·635		1·453
1	332·0	1·330	0·010308	−1·9868	2·004		1·504		2·00	
				dl-Camphorquinone. M = 166. Solvent—Chloroform.						
1	332·0	1·330	0·010548	−1·9768	2·004		1·504		2·00	
						1·329		1·591		1·453
2	249·0	1·362	0·008751	−2·0580	1·348		1·101		1·50	
						1·506		1·763		1·549
3	166·0	1·394	0·007030	−2·1530	0·814		0·717		1·00	
						1·667		1·852		1·568
4	83·0	1·420	0·005879	−2·2307	0·374		0·352		0·50	
						1·553		1·620		1·407
5	41·5	1·430	0·005398	−2·2678	0·180		0·175		0·25	
						1·444		1·656		1·467
1	332·0	1·330	0·010548	−1·9768	2·004		1·504		2·00	

TABLE VIII.

Viscosity of Solutions in Poises (Temp. 35°).

$$100\ \eta^{\frac{1}{3}} = (100 - x)\eta_1^{\frac{1}{3}} + x\eta_2^{\frac{1}{3}}$$

No.	Molecular per cent. of solute in solution (x)	η (Obs.)	η_2 (Calc.)
d- and *l*-Sodium Camphorate in Water (*cf.* Table III).			
1	0·788	0·011366	73·96
2	0·507	0·009575	61·63
3	0·377	0·008955	63·86
4	0·184	0·007975	51·11
5	0·091	0·007570	43·88
6	0·00	0·007225	
d- and *l*-Camphoric Acid in Ethyl Alcohol (*cf.* Table II).			
1	6·595	0·020289	1·61
2	5·495	0·017726	1·50
3	4·229	0·015157	1·15
4	3·115	0·013253	1·28
5	1·204	0·010532	1·11
6	0·599	0·009817	1·05
7	0·298	0·009388	0·47
8	0·00	0·009165	
d- and *l*-*Iso*nitrosocamphor (stable) in Ethyl Alcohol (*cf.* Table IV).			
1	6·479	0·014146	0·36
2	3·085	0·011764	0·51
3	1·509	0·010524	0·64
4	0·744	0·009948	0·97
5	0·371	0·009476	0·59
6	0·00	0·009165	

TABLE VIII—(*Contd.*).

Viscosity of Solutions in Poises (Temp. 35°).

$100\eta_3^{\frac{1}{3}} = (100 - x)\eta_1^{\frac{1}{3}} + x\eta_2^{\frac{1}{3}}$

No.	Molecular per cent. of solute in solution (x)	η (Obs.)	η_2 (Calc.)
	***d*- and *l*-Camphorquinone in Chloroform** (*cf.* Table VII).		
1	19·32	0·010308	0·0736
2	13·87	0·008615	0·0774
3	8·86	0·007028	0·0736
4	4·28	0·005870	0·0773
5	2·11	0·005363	0·0835
6	0·0	0·004859	
	***d*- and *l*-Camphor in Ethyl Alcohol** (*cf.* Table I).		
1	14·72	0·011765	0·0368
2	11·57	0·011145	0·0363
3	1·20	0·009712	0·1656
4	0·29	0·009573	2·0260
5	0·00	0·009165	

Summary.

The viscosity-concentration data for the *d*-, *l*- and *dl*-forms of camphor, camphoric acid, sodium camphorate, *iso*nitrosocamphors and camphorquinone have been analysed, and the following conclusions may be drawn :—

(1) The simple mixture rule does not apply as the viscosity-composition graphs are not linear.

(2) The formula of Kendall, involving the cube root of viscosity does not apply to the data given in this paper : the calculated values of the " Viscosity " of the solute are very variable, except in the case of camphorquinone in chloroform.

(3) The logarithmic viscosity formula of Arrhenius gives satisfactory results in all cases except with *iso*nitrosocamphors. The density-composition graph of *iso*nitrosocamphor departs from linearity, indicating a volume change, and this may account for the non-applicability of the Arrhenius' formula.

(4) The formula of Arrhenius fits in better with observations, when the concentration is expressed in moles per 1000 g. of *solvent*, rather than moles per 1000 g. or 1000 c.c. of *solution*. There is, however, one exception in camphorquinone, whose chloroform solutions give better agreement with the Arrhenius' formula when the concentration is expressed as moles per 1000 c.c. of solution. The density-composition graph of these solutions is not linear.

(5) The applicability of the Arrhenius' formula is also illustrated by plotting $\log\eta$ against molecular concentration, expressed as under (4), when straight lines are obtained.

ON THE MIQUEL-CLIFFORD CONFIGURATION.

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1. *Introduction.*

The classical chain of theorems connected with the names of Miquel and Clifford associate with an even number of lines in a plane a point, called their "Miquel Point", and with an odd number of lines a circle, called their "Clifford Circle", with the well-known incidence relations between them. The resulting configuration could be viewed from the standpoint of the projective geometry of the plane, or as one belonging to inversive geometry. Clifford's own proof was based on considerations connected with the foci of n-fold parabolas and belongs to the former category.[1] It was, however, pointed out by J. H. Grace[2] and later by E. H. Neville[3] that if the n straight lines which generate the figure be placed by concurrent circles, the configuration becomes symmetric in the sense that it consists of 2^{n-1} circles and 2^{n-1} points such that n of the circles pass through each point and n of the points lie on each circle. It would thus appear, that it would be more appropriate to view it as one of circle (inversive) geometry, and I have recently[4] discussed from this standpoint certain transformations in circle-space connected with the configuration.

In this paper it is seen that by combining both these points of view, fresh light is thrown on the structure of the configuration. The results obtained are :

(i) a proof of the following theorem announced without proof[5] by the late V. Ramaswami Aiyar, Founder of the Indian Mathematical Society,—" The curves that I desire to bring to the notice of the reader are of class $n + 1$. Each touches the line at infinity n times—the circular points at infinity being always two of the points

[1] W. K. Clifford, "Synthetic Proof of Miquel's Theorem", *Mathematical Papers*, p. 38.

[2] Grace, "Circles, Spheres and Linear Complexes", *Trans. Camb. Phil. Soc.*, 1898, **16**, 31.

[3] Neville, "The Inverse of the Miquel-Clifford Configuration," *Jour. Ind. Math. Soc.*, 1926, p. 241.

[4] A. Narasinga Rao, "On certain Cremona-Transformations in Circle-Space connected with the Miquel-Clifford Configuration," *Proc. Camb. Phil. Soc.*, 1937, **33**, § 31.

[5] V. Ramaswami Aiyar, "Note on a Class of Curves," *The Mathematics Student*, 1936, **4**, p. 106.

at contact. It can be determined when $2n$ tangents are assigned. If $2n + 1$ tangents of such a curve be taken, the Clifford-Miquel Circle of the $2n + 1$ tangents becomes A STRAIGHT LINE";

(ii) a generalisation of Ramaswami Aiyar's result to cover the case when the Clifford Circle of the $2n + 1$ lines is a circle cutting a fixed circle orthogonally, or is of constant radius;

(iii) a proof that at each of the points of multiple incidence in the configuration, the concurrent circles cut at the same angles as at any other of these points.

2. *The Projective View-point.*

Let p be the projective plane with a degenerate Caylean Absolute consisting of two points I, J. The line IJ is the "line at infinity" and any conic through I and J is a "circle".

Let (1) and (2) denote two circles through a point O which will also be denoted by the symbol ( ). Their other intersection (12)[6] is the Miquel Point of (1) and (2). With three circles (1), (2), (3) we have three such points (12), (23), (31) which lie on the Clifford Circle (123). If however, (3) is a singular circle through O consisting of the line OI and a line l_j through J, the intersections (31) and (32) (other than O, I, J) are on l_j so that the circle (123) breaks up into l_j and the line joining the Miquel Point (12) to I.

With four circles through O, one of which, say (4), consists of OI and l_j we have one proper Clifford Circle (123) and three degenerate Clifford Circles each of which breaks up into l_j and another line. The Miquel Point (1234) common to all these circles is thus the intersection of l_j with (123), other than J. Thus, if we take five circles of which (5) breaks up into OI and l_j, four of the Miquel-points lie on l_j. Hence the Clifford Circle of the five concurrent circles breaks up into and l_j the join of (1234) with I. It is easy to see that these considerations may be indefinitely extended and apply to either circular point. Hence,

Given an even number of circles (1), (2), (3), $\cdots\cdots(n)$ through O they have a Miquel Point M $\equiv (12\cdots n)$. With every additional circle (x) through O may be associated the Clifford Circle $(123\cdots nx)$ through M. When (x) breaks up into OI and a line l_j through J, the associated circle $(12\cdots nx)$ breaks up into l_j and the line MI. .. $(2 \cdot 1)$

It is thus seen that point-circles through O correspond to point-circles through M. Among the circles through both O and M, there are two which are

[6] Both here and throughout this paper the order of the letters in a bracket is a matter of indifference. The notation is that of my paper on *Cremona Transformations*, etc.

point-circles. These points will be called the " cross-pair " of O and M and denoted by C and C′. They stand respectively for the line pairs OI, MJ and OJ, MI. We shall now prove that

if the additional circle (x) through O be either of the point-circles C or C′ (the cross-pair of O and M), the associated Clifford Circle $(12\cdot\cdot\cdot\cdot nx)$ is the point-circle at M. .. .. $(2\cdot 2)$

This follows from $(2\cdot 1)$ since C is the line pair OI, MJ so that the associated Clifford Circle is MI, MJ. Similarly for C′.

3. *The Inversive View-point.*

It is known that the geometry of the plane under the inversion group is isomorphic with the projective geometry of a 3-space S_3 with an invariant quadric Ω whose points represent the point-circles on the plane. The point-circles O, M on p are represented by points o and m on Ω while the two groups of circles (1), $(2)\cdot\cdot\cdot\cdot(n)$ and $(23\cdot\cdot\cdot\cdot n)$, $(13\cdot\cdot\cdot\cdot n)$, $\cdot\cdot\cdot\cdot\cdot(12\cdot\cdot\cdot\cdot n-1)$ which pass respectively through O and M are represented by points on the tangent planes π_0 and π_m to Ω at o and m. The intersection of the two tangent planes represents the circles in p through O and M, and the two points c, c' where the line cuts Ω correspond obviously to the cross-pair C, C′ of O, M. We shall use the bracket symbols to represent both the circle on the plane p and the representative point in S_3.

By $(2\cdot 1)$ we have for every point (x) on π_0, an associated point $(12\cdot\cdot nx)$ on π_m. In my paper on *Cremona Transformations* cited earlier, I have discussed the transformation $(x)\longrightarrow(12\cdot\cdot\cdot\cdot nx)$ and shown that

(i) it is an involutoric transformation of order $t+1$ (where $n=2t$) of the De Jonquiere type .. .. $(3\cdot 1)$

(ii) its F-elements of unit multiplicity in the two planes are the points $(1)\,(2)\cdot\cdot\cdot\cdot(n)$ and $(23\cdot\cdot\cdot\cdot n), (13\cdot\cdot\cdot\cdot n), \cdot\cdot\cdot\cdot\cdot(12\cdot\cdot\cdot\cdot n-1)$ and its elements of multiplicity t are O = ( ) and M = $(12\cdot\cdot\cdot\cdot n)$; .. .. $(3\cdot 2)$

so that

(iii) the P-curve corresponding to (r) in π_0 is the line joining M to $(12\cdot\cdot\cdot r-1\ r+1\cdot\cdot\cdot\cdot\cdot n)$ on π_m .. .. $(3\cdot 3)$

(iv) while the P-curves of O and M are curves of order t on π_m and π_0 having m and o for singular points of order $t-1$ .. $(3\cdot 4)$

It follows from $(3\cdot 2)$ that a line through O in π_0 say the join of O and (x) is transformed into a line through M in π_m namely, the join of M and $(12\cdot\cdot\cdot nx)$; when (x) approaches any point on the line O (r) so that O (x) tends

to O (r), the corresponding line through M should by $(3 \cdot 3)$ approach the join of M and $(12 \cdot \cdot \cdot \cdot r-1 \quad r+1 \cdot \cdot \cdot \cdot n)$. Hence

The pencil of lines through o in the plane π_0 is in one-one correspondence with the pencil of lines through m in π_m which are their transforms. To the line joining o to (r) corresponds the join of m with the associated Miquel Point $(12 \cdot \cdot \cdot \cdot r-1 \quad r+1 \cdot \cdot \cdot \cdot n)$. The generators oc, oc' correspond respectively to the generators mc' and mc. $(3 \cdot 5)$

The last statement follows from the following considerations: Since c represents the circle OI, MJ and o the circle OI, OJ the points on the line oc correspond to the circles of the pencil OI, l_j where l_j is any line through J. Similarly points on mc' represent the pencil of circles MI, l_j. From $(2 \cdot 1)$ it follows that points on oc correspond to points on mc'. A similar proof holds for oc' and mc.

From $(2 \cdot 2)$ it follows that the P-curves of o and m pass through both c and c'. Let q and q' be points on the planes π_0 and π_m corresponding each to the other in the involutoric Cremona Transformation. As q' approaches any point on the P-curve of o, q approaches o in a particular direction. When q' approaches c, Mq' tends to Mc and hence by $(3 \cdot 5)$ oq tends to oc'. Also by $(2 \cdot 2)$, q tends to the limit o. Hence

The P-curves of o and m pass through both c and c'. The transform of a curve in one of the planes, say π_m which passes through c (or c') is a curve in the other plane π_0 having a singular point at o, one of the tangents at o being the generator oc' (or oc). .. .. $(3 \cdot 6)$

4. *Applications.*

Consider now the transform of the line cc', the intersection of π_0 and π_m, which represents the circles in p through O and M. Regarded as a line in π_m, it is the transform of, or transforms into, (since the transformation is involutoric) a curve Γ_0 of degree $t+1$ in π_0 having by $(3 \cdot 2)$, a singularity of order t at o with mc and mc' as two of the nodal tangents (by $3 \cdot 6$), and passing through the points (1) (2) $\cdot \cdot \cdot \cdot (n)$. If we take o to be the point on Ω representing the " point-circle at infinity, " the points on Γ_0 correspond to straight lines on p which envelop a curve of class $t+1$ having the line at infinity (which corresponds to o) as a multiple tangent of order t, two of the points of contact being the circular points I and J, and also touching the lines (1) (2) $\cdot \cdot \cdot \cdot (n)$. When another tangent (x) to such a curve is taken, their Clifford Circle $(12 \cdot \cdot \cdot nx)$ being the transform of (x) corresponds to a point on cc', that is, it is a straight line through M. Thus the Clifford Circle of any $n+1 = 2t+1$ tangents to such a curve is a straight line, and this is precisely Ramaswami Aiyar's Theorem mentioned in the introduction.

More generally, if the Clifford Circle $(12\cdot\cdot\cdot\cdot nx)$ is to cut a given circle orthogonally, (x) must lie on a curve in π_0 which is the transform of a straight line on π_m. Such a curve is of class $t+1$ with a node of order t at o and passes through $(1)\cdot\cdot\cdot(n)$, but it will not have oc and oc' for nodal tangents. Interpreting in terms of lines in plane p with o corresponding to the line at infinity, we have the following result :—

> Let Γ be an t-fold parabola (a curve of class $t+1$ touching the line at infinity t times) and $(1)\ (2)\cdot\cdot\cdot\cdot(2t)$ denote $2t$ tangents to it. If (x) be any variable tangent to Γ, the Clifford Circles $(123\cdot\cdot\cdot\cdot 2tx)$ will for all positions of (x) be orthogonal to a fixed circle. $(4\cdot 1)$.

Finally, let us determine the relation between $2t+1$ lines so that their Clifford Circles may be of given radius.

Now circles of constant radius on p correspond to points on a quadric Ω_1, touching Ω at the " point-circle at infinity " which we take to be o. Since Ω_1 belongs to the linear system containing Ω and the squared tangent plane π_0, its section by π_m belongs to the linear system containing the line pair mc, mc' and the squared line cc'. Hence the section of Ω_1 by π_m is a conic touching mc and mc' at c and c'. Different conics of this linear system correspond to different values of the radius.

In order that the Clifford Circle $(12\cdot\cdot\cdot\cdot nx)$ may be of fixed radius, (x) must lie on the locus γ in π_0, which is the transform of a conic touching mc and mc' at c and c'. It is a curve of degree $2t+2$ having o for a singular point of order $2t$ and the points $(1)\ (2)\ldots.(n)$ for double points. Since the conic passes through c and c', its transform γ has by $(3\cdot 6)$ the generators oc and oc' for two of the tangents at the node. By $(3\cdot 5)$ the other intersections of the conic with mc and mc' go over into points on oc' and oc, and as these are also located at c and c', it follows that oc and oc' are inflexional tangents at o to two of the branches through it.

When the points of γ are interpreted as lines in p, o corresponds to the line at infinity and the intersections of γ with the generator oc (or oc') to the tangents from the circular points I (or J) to the envelope of the lines. The inflexional tangents oc, oc' thus imply that three of the tangents from I and J are coincident with the line at infinity, *i.e.*, I and J are cusps with the line at infinity for the cuspidal tangent in each case. Hence we have the result :—

> Given a curve of class $2t+2$ having the $2t$ lines $(1)\ (2)\cdot\cdot\cdot\cdot\cdot(2t)$ for bitangents and the line at infinity as a singular line of order $2t$, being the cuspidal tangent at the circular points I and J, if (x) be any variable tangent to the curve, then the Clifford Circle $(12\cdot\cdot\cdot\cdot 2mx)$ is of constant radius. .. .. $(4\cdot 2)$

5. *Other Applications. Angle Properties.*

We have seen (3·5) that the lines of the pencil vertex o in π_0 are in projective correspondence with the lines of the pencil vertex m in π_m.

If

we make the convention that any figure repeated twice in a bracket symbol destroys itself and may be omitted altogether, .. (5 · 1)

so that we have $(23 \cdot \cdot \cdot \cdot n) \equiv (123 \cdot \cdot \cdot \cdot n\ 1)$, the correspondence is concisely expressed by the statement that

for all values of x ($x \leqslant n$ and $x > n$) the line in π_0 through (x) corresponds to the line in π_m through $(12 \cdot \cdot \cdot \cdot nx)$ .. .. (5 · 2)

Now a line through o corresponds in p to a pencil of circles touching one another at O and so determines a line element at O. We thus have a correspondence in p between the line elements at O and M. With the isotropic line element along OI is associated the pencil of circles OI, l_j and we have seen in (2·1) that the corresponding circles through M belong to the pencil MI, l_j. Hence the isotropic directions OI, OJ correspond to MI, MJ and it follows that

the angle between (r) and (s) is equal to the angle between $(12 \cdot \cdot \cdot nr)$ and $(12 \cdot \cdot \cdot \cdot ns)$. .. .. (5 · 3)

The equality is a direct equality and not an inverse equality (since OI corresponds to MI and OJ to MJ), so that a rotation through a suitable angle $\theta_{12 \cdot \cdot \cdot n}$ will carry the line elements at O into those at $M = (12 \cdot \cdot \cdot \cdot n)$.

The equality of the angles formed by the line elements at the various points of multiple incidence holds not only for extreme points like O and M, but also in the case of any two of them. Thus take the point (123456). This is the Miquel Point of (1) (2) (3) (4) (5) (6) through ( ), and hence by (5·3), the angle betweeen (r) and (s) is the angle between $(12 \cdot \cdot \cdot \cdot r - 1\ r + 1 \cdot \cdot \cdot \cdot 6) = (12 \cdot \cdot \cdot \cdot 6r)$ and $(12 \cdot \cdot \cdot s - 1\ s + 1 \cdot \cdot \cdot \cdot 6) = (12 \cdot \cdot \cdot 6s)$ provided $r, s \leqslant 6$. If $r > 6$, (r) is no longer a singular element of the Cremona Transformation between the tangent planes π_0 and π_t to Ω at o and $t = (12 \cdot \cdot \cdot 6)$, but (r) is carried over into $(12 \cdot \cdot \cdot \cdot \cdot 6r)$ and hence by (3·5) the line elements correspond. Thus with the convention (5·1) we may assert that there is a single projective correspondence in which the line element of (r) through O corresponds to the line element of $(12 \cdot \cdot \cdot \cdot 6r)$ through t, r taking all the values $1, 2 \cdot \cdot \cdot \cdot n$. Hence the result.[7]

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[7] *Vide* A. Narasinga Rao, "The Miquel-Clifford Configuration in the Geometries of Mobius and Laguerre," *Annamalai University Jour.*, VII, 1937.

The angles formed by the line elements of the n circles which meet at any point of multiple of incidence is the same for all such points. The line elements at any such point can be carried over into the corresponding line elements at any other point by a pure rotation. .. (5·4)

This may be regarded as a generalisation of the well-known result that the angle between a tangent to a circle and a chord through the point of contact is equal to the angle in the opposite segment. For, when $n = 2$ and we start with two straight lines (1) (2) meeting at (12), the transform of a third straight line (3) is the circumcircle (123). Now (5·4) asserts that the angle between say (2) and (3) at the point-circle at infinity of the tetracyclic plane, [whose magnitude may be taken to be the angle between the lines (2) and (3) since two circles cut at the same angle at both intersections] is equal to the angle between their transforms (122) = 1 and (123).

Summary.

In this paper the Miquel-Clifford configuration is studied both from the standpoint of the projective geometry of the plane and of Mobius Geometry —the inversive geometry of the plane. By combining both view-points conditions are obtained for the Clifford Circle of $2t + 1$ lines to be (i) a straight line, (ii) a circle of given radius. It is also shown that at each of the points of multiple intersection of the configuration the concurrent circles cut at the same angles as at any other of these points.

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